TEXTURE CONTROL IN PROCESSING OF HIGHLY ORIENTED MESOPHASE-BASED GRAPHITE (HOMG) TAPES

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Introduction

It has recently been shown that highly graphitising, highly oriented mesophase pitch-based carbon tapes can be produced [1]. The tapes are promising for thermal management applications. It has also been shown that the orientation of the graphite planes relative to the plane of the tape can change from parallel to perpendicular according to the processing conditions during tape formation. This paper reports how the transverse texture is controlled by adjusting shear rate in the extrusion die with a large aspect ratio.

Experimental

ARA 24 naphthalene-derived synthetic mesophase pitch was used as a starting material. The mesophase pitch tape was prepared by melt extrusion through a slot-shaped die, which has a profile entry leading to a slot with an aspect ratio of 50. The as-extrudate (drawn only by its own weight) and pitch tape (drawn by a winder) were examined by both optical microscopy and XRD texture scan [2] to characterise the preferred orientation and transverse arrangement of the polyaromatic discotic molecules of the mesophase pitch. Some circular pitch fibres were also spun and their preferred orientations were measured for the purpose of comparing with tapes.

Results and discussion

Preferred orientation along the tape

Shear flow during spinning induces the alignment of discotic mesophase molecules in pitch fibre, which determines the axial preferred orientation and the microstructure of the finished carbon fibres, and this in turn influences the macroscopic properties [3]. Therefore, it seems reasonable to use shear rate to examine its relation to the orientation of discotic mesophase molecules in pitch as-extrudate and the resultant pitch tapes. The hydraulic radius and depth of the extrusion die govern the shearing process, therefore, appropriate design of die geometry is important. The shear rate at the surface of the slot-shaped die can be controlled by varying the extrusion temperature and pressure.

Fig. 1 shows the degree of preferred orientation (FWHM value) of as-spun mesophase pitch tapes as a function of their average transverse areas. The circular fibres are also plotted in the figure for comparison (the numbers in the figure indicate the diameters of circular fibres). It is evident that the preferred orientation of as-spun mesophase pitch circular fibres improves significantly as the transverse areas increases from 100 to 2000 $(\mu m)^2$. A further increase of fibre transverse areas shows a lower effect on the preferred orientation of mesophase molecules along the fibre axis. In the case of the as-spun mesophase tapes, their transverse areas can be made significantly larger than circular fibres. It is interesting to note that the preferred orientation of typical mesophase pitch tapes is comparable to mesophase pitch fibres of the largest possible diameter. The as-extrudates from slot-shaped die (drawn only by their own weight) show a low degree of preferred orientation with FWHM values ranging from 37-42^o. This result agrees with the low degree of axial preferred orientation of as-extrudate from a circular die. The lower degree of preferred orientation of the as-extrudate in the shear flow direction is probably caused by the "die swell". The drawing process significantly improves the preferred orientation of the tape in comparison with that of as-extrudates. However, the sharp deterioration of the preferred orientation with increase of drawing speed as in the case of circular fibres has not been observed for as-spun tapes probably due to a lower drawing speed required during tape formation, which prevents the introduction of disorder of the discotic mesophase molecules.

Transverse texture of the tapes

It has been noted that different transverse textures can be developed for circular mesophase pitch-based carbon fibres [4]. It was discovered in this study that the transverse textures of the tapes could be controlled by shear rate. Generally speaking, line-origin transverse textures develop when tapes are produced at high shear rate, i.e. > 6000 s^{-1}. Meanwhile, when tapes are produced at low shear rate (<4000 s^{-1}) a novel transverse texture develops with layer planes predominantly arranged parallel to the tape surface. Less clearly defined transverse textures can develop at intermediate shear rate.

It is believed that the different transverse textures are induced during shear flow, and the developed transverse textures are further enhanced by extensional flow before solidification during tape winding up. The as-extrudates only drawn by their own weight were examined by optical microscopy, SEM and XRD texture scans. The low shear rate (~2820 s^{-1}) as-extrudate has a bigger transverse area than that of the high shear rate as-extrudate (~11510 s^{-1}). The alignment of discotic mesophase molecules within the transverse area of the as-extrudates was assessed by polarised light optical microscopy. The low shear rate as-extrudate had a more parallel arrangement of the discotic molecules with respect to the main surface of the as-extrudate than that of the high shear rate as-extrudate. After a closer inspection, it appears that the major difference lies in the two perpendicular alignment regions, which are narrower in the low shear rate as-extrudates.

Since it is difficult to quantify the discotic molecular arrangement by optical microscopy, the XRD texture scan was employed. It reveals an overall different arrangement of the discotic molecules in the as-extrudates obtained under different shear rates.

The drawing process improves the preferred orientation along the tape axis, but it has not significantly changed the transverse texture when tapes are produced at high shear rate. However, it was found that the appropriate degree of drawing enhances the parallel layer arrangement when tapes are produced at low shear rate. Both cases have been clearly demonstrated by XRD texture scans; the as-spun tapes collected on the roller have very similar vertical molecular arrangement to that of the as-extrudate in the case of high shear rate, while the as-spun tapes have enhanced parallel molecular alignment compared with their corresponding as-extrudates at low shear rate. XRD pole figures can not provide information on the distribution of different alignment of discotic molecules, which can be complemented by optical or scanning electron microscopy. Of course, SEM is unable to reveal the molecular arrangement in as-spun tapes, however, it can reveal the carbon layer alignment once the tapes are carbonised provided that the discotic molecular arrangement is completely fixed by stabilisation and there is no molecular rearrangement during stabilisation and subsequent carbonisation treatment.

The same shear rate can be achieved by combining different extrusion pressure and temperature, especially in the case of low shear rate. Two tapes were produced under the same shear rate of about 2820 s^{-1} obtained at 290^{o}C/8 bar and 280^{o}C/25bar, respectively. The same wind-up speed was used and SEM observation shows they have similar average value of transverse areas. The XRD texture scans show that both tapes have similar transverse textures, indicating that the transverse textures are shear rate dependent regardless of the extrusion temperature. However, the preferred orientations of the two tapes are different; the tape obtained at 290^{o}C/8 bar has better preferred orientation (FWHM reduced by ~4^{o}). This result is in agreement with that of circular as-spun mesophase pitch fibres; it was found that circular fibres of the same diameter have better preferred orientation if they are melt spun at higher spinning temperature [5]. Apparently, the lower viscosity at higher spinning temperature makes the discotic mesophase molecules align more parallel to the fibre or tape axis.

The XRD texture scans of as-spun tapes obtained at the same temperature with different transverse textures show that they have similar degrees of preferred orientation along the axis of the tape, demonstrating that the axial preferred orientation of the discotic mesophase molecules is not dependent on the shear rate.

Conclusions

Discotic liquid crystalline mesophase molecules will line up during shear flow in the slot-shaped die. The as-extrudate without drawing (except under its own weight) exhibits a low degree of preferred orientation, characterised by FWHM. This preferred orientation can be significantly improved by drawing, thereby a mesophase pitch-based tape is produced. The as-spun tapes have a high degree of preferred orientation, comparable to that of large diameter circular as-spun pitch fibre. It was found in this study that the transverse textures of the tapes could be controlled by shear rate; the high shear rate gives a line-origin orientation whereas the low shear rate produces a novel transverse structure with the discotic mesophase molecules predominantly oriented parallel to the tape surface.

References

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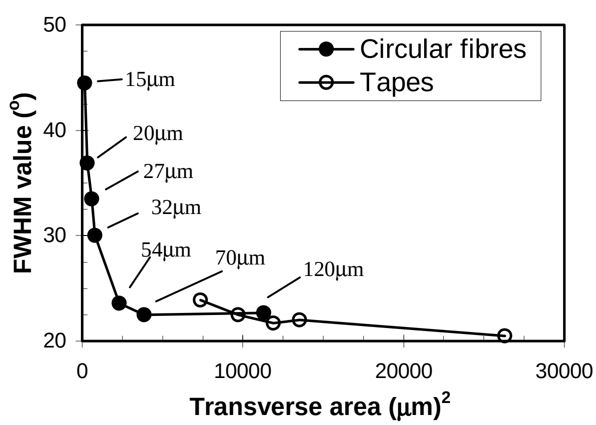

Fig. 1. Preferred orientation of the as-spun circular fibres and tapes as a function of transverse areas.