J Mater Sci (2006) 41:5687–5695
DOI 10.1007/s10853-006-0330-2

A new shear technique: Semi Continuous Shear Flow (SCSF) in medium and ultra high molecular weight Polyhydroxybutyrate blends

Lakshmi Sharma · Yoshino Ogino · Toshiji Kanaya · Tadahisa Iwata · Yoshiharu Doi

Received: 5 August 2004 / Accepted: 19 August 2005 / Published online: 28 June 2006
© Springer Science+Business Media, LLC 2006

Abstract In MMWT/UHMWT PHB blends (99.5/0.5), (99/1), (98/2) and (97/3) we demonstrate that by applying our new shear technique, ''semi continuous shear flow'', copious fibre formation is guaranteed, irrespective of the ultra high molecular weight composition. The shishes formed via this technique are extremely stable being able to maintain their stability for at least 5–10 min. When this technique was applied to MMWT/UHMWT PHB blends of compositions (95/5), (90/10) and (85/15) disorientated fibres were observed in the flow direction. On increasing the UHMWT component, distinct unordered and intertwining of fibres resulted and with severe shearing orientation occurred, however shish formation was limited. We propose the optimum conditions for shish formation and the critical molecular weight necessary for entanglement.

Introduction

PHB is a natural biopolymer and its unique biodegradable and plastic properties have established it as a major environmentally friendly polymer for packaging and biomedical applications [1, 2]. However, a severe drawback of PHB, which limits its usage, is that over time PHB becomes brittle, a process known as embrittlement [3–6]. We can manipulate the natural spherulitic PHB morphology, by using high compositions of the ultra high molecular weight (UHMWT) PHB under shear process conditions. The resultant flow morphology is anticipated to be highly orientated, this ordered structure will introduce new properties and applications, whilst removing or severely lessening PHB's embrittlement. Currently studies on shear flow of PHB attaining a shish kebab morphology have only been investigated by our group [7–8].

In our initial studies [7], we employed rheo-SAXS, rheo-light scattering and rheo-optical methods to investigate the polyhydroxybutyrate (PHB) morphology under varying shear flow conditions. In these studies of the homopolymer, medium molecular weight PHB, M_w 360,000, at high shears, only the initial stages of shish formation (i.e. incomplete shish formation) and a definite kebab morphology was identified, we term this a partial shish kebab morphology [7, 8]. From our findings, we proposed that a stable shish (complete shish formation) could be achieved using high shears and ultra high molecular weights (UHMWT).

We also investigated medium (MMWT M_W 360,000)/ultra high (UHMWT M_W 5×10^6) molecular weight PHB blend using rheo-optical and rheo light scattering. We predicted that by introducing the ultra high molecular weight species extreme stability to the shish kebab structure would occur via highly orientated polymer chains [8]. For the MMWT/UHMWT PHB blends at (99.5/0.5) and (99/1), we observed row nuclei, with phenomenally increased nucleation and crystallisation, and only the initial stages of shish formation (we term a

L. Sharma (✉) · Y. Ogino · T. Kanaya
Polymer Material Science Laboratory, Institute for Chemical Research, Kyoto University, Kyoto, Uji City, 611 0011, Japan
e-mail: lsharma@pmsci.kuicr.kyoto-u.ac.jp

T. Iwata · Y. Doi
Polymer Chemistry Laboratory, RIKEN Institute (The Institute of Physical and Chemical Research), Hirosawa, Wako-shi, Saitama 351-0198, Japan

partial shish) were observed. At the higher compositions, (98/2) and (97/3) we noticed the immediate formation of fibres with complete shish formation evident. Thus we concluded that on maintaining identical shear rates the row nuclei length increases and becomes more fibrous on increasing the UHMWT species, this micro-level fibre morphology is crucial to achieving and sustaining the shish kebab, where its existence is composition and molecular weight dependent.

In this paper, we will investigate two methods which we suspect will not only guarantee but will maintain the shish kebab morphology in PHB UHMWT blends. Our aim is to devise a new shear technique and combine this with the rheo-light scattering and rheo-optical microscopy. By manipulating the shear flow, we can achieve the maximum stability for the shish kebab, gaining further insight into its origins. Previously this manipulation was attempted by Kornfield's group [9, 10] on a series of petroleum based polymers where short pulsed shear was applied, however, this did not provide the optimum shish kebab hold conditions and stability was not achieved for a lengthy period. Our method involves specifically timed shear which we term the semi-continuous shear flow (SCSF), this method should guarantee the shish kebab existence irrespective of the amount of UHMWT species in the blend.

Previous studies have investigated the relationship between molecular weight and shear at low blend compositions and this has mainly focused on polypropylenes and polyethylene based polymers [11–19]. These studies concluded that the high molecular weight species enhances crystallisation kinetics and melt orientation, explained by the slow relaxation of polymer coils to the random state. This orientation state is fundamental to the resultant morphology. In this research, we will apply the semi-continuous shear method to the MMWT/UHMWT PHB blends, (95/5), (90/10) and (85/15), at the optimum shear rate of 100 s^{-1} for 1 s. This allows one to determine the polymer morphology for a given molecular weight under shear in PHB blends, so establishing the maximum conditions for shish kebab morphology.

By understanding these rheological characteristics and applying these to the polymer industrial processing a wide range of properties and commercial applications can be achieved whilst reducing PHB's embrittlement. In essence a ''new'' PHB material will be born.

Experimental part

Polyhydroxybutyrate, $M_w = 360{,}000$, was purchased from Aldrich Chemicals, Japan.

Ultra high molecular weight biosynthesis preparation

The UHMWT PHB, $M_w = 5 \times 10^6$, was biosynthesized from glucose using recombinant *E. coli* XL-1 blue (PSY l105) bacterium harbouring *R. eutropha* H16 PHB biosynthesis phbCAB genes [20]. The resultant material was reprecipitated in *n*-hexane from chloroform solution and dried in vacuo for a period of 1 week [21].

Blend preparation

The blends were prepared with the UHMWT at 0.5, 1, 2 and 3% composition, to the blend weights, hot chloroform was added with continual heating and stirring to aid dissolution. These solutions were then left for a week, guaranteeing complete dryness, and then pressed at 180 °C and used in this state for analysis.

Rheo-DPLS

The shear cell Linkam CSS-450 was connected to a depolarized light scattering (DPLS) apparatus with He–Ne laser light source (wavelength $\lambda = 632.8$ nm) covering a range of scattering vector Q of 5×10^{-4} to $3.18 \times 10^{-3} nm^{-1}$ to determine the formation of shish in PHB. All samples were analyzed at 100 s^{-1} shear for 1 s with a 300 μm gap keeping a constant strain of 3300%.

Rheo-microscopy

The micro level collection of shish kebab structures was analyzed by using a shear flow cell, details as rheo-DPLS, connected to an optical microscope Olympus BX50 with video attachment. The resultant morphology was measured at 100, 70, 50, 35 and 10 s^{-1} shear rate with corresponding times 1, 1.42, 2, 2.85 and 10 s, respectively with a 300 μm gap keeping a constant strain of 3300%.

Semi Continuous Shear Flow (SCSF)

The circular discs of pressed PHB blends were placed in the flow cell and heated to 190 °C for 1 min, to melt and remove any previous thermal history, and then cooled to crystallise isothermally at 130 °C. The shear technique applied, we have termed as ''semi continuous'', involves an initial shear until the appearance of the nuclei. Here, the second shear is applied, after which subsequent shearing occurs. For light scattering, we cannot visualise the nuclei formation, therefore, we

account for this by approximately 10 s intervals between shears.

Results and discussion

Using MMWT/UHMWT PHB blends, we developed a new technique of applying shear flow, ''semi-continuous'' shear, where fibre formation was achieved for all blend compositions. This could not be achieved using using the normal shear technique on PHB [7].

In these studies, each fibre has a phenomenal length with its edges assuming a cuboidal configuration, Figs. 1–4. In some cases, spherulites were also present among the fibres, this was attributed to shearing too late when spherulite nuclei had already developed. However, this is extremely difficult to avoid since not all nuclei in the sample can be immediately identified before the next shear is applied, resulting in the already developed spherulite appearing in the flow.

With increasing the ultra high molecular weight component in the blend, the number of continual shears required to completely achieve fibre formation decreases, i.e. with the higher molecular weight compositions a well developed fibre appears on just a single shear. This is expected since the low compared to the higher molecular weight species becomes non-orientated rapidly.

Interestingly, we noticed that when a spherulite was present in the shear path, the fibre splits in two before the spherulite and rejoins again after this imposition, Fig. 1b. This suggests that the growth or laying down of the shish is affected by the surrounding medium. Based on previous findings by Keller [22, 23] one would expect the shish to over-lay the spherulite. However, according to the Janeschitz-Kriegl model [24, 25], where the precursors are laid down point to point, this surface anomaly would be expected.

Too many shears, usually 4–6 shears maximum, causes the material to form ''break lines'' around its fibres and on successive shears the material will completely tear at these points. The nuclei are still functional, despite the material tearing, forming row nuclei and random spherulites. Additionally, on this excessive shearing, the resultant fibres displayed many horizontal

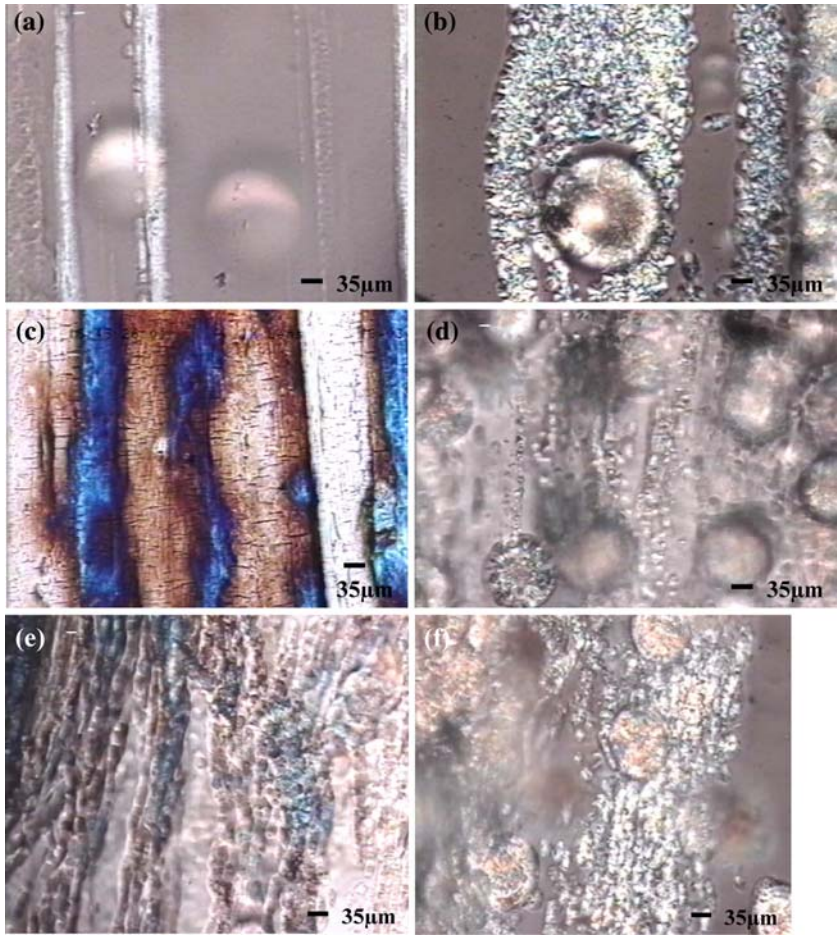

Fig. 1 Rheo-optical micrograph of (**a**) MMWT PHB at the second shear on the applied shear rate of 50 s^{-1} for 2 s; (**b**) MMWT/UHMWT PHB (99.5/0.5) at the fourth shear on the applied shear rate of 35 s^{-1} for 2.85 s; (**c**) MMWT/UHMWT PHB (99.5/0.5) at the third shear on the applied shear rate of 100 s^{-1} for 1 s; (**d**) MMWT/UHMWT PHB (99/1) at the third shear on the applied shear rate of 10 s^{-1} for 10 s; (**e**) MMWT/UHMWT PHB (99/1) at the second shear on the applied shear rate of 70 s^{-1} for 1.42 s; (**f**) MMWT/UHMWT PHB (99/1) at the third shear on the applied shear rate of 10 s^{-1} for 10 s

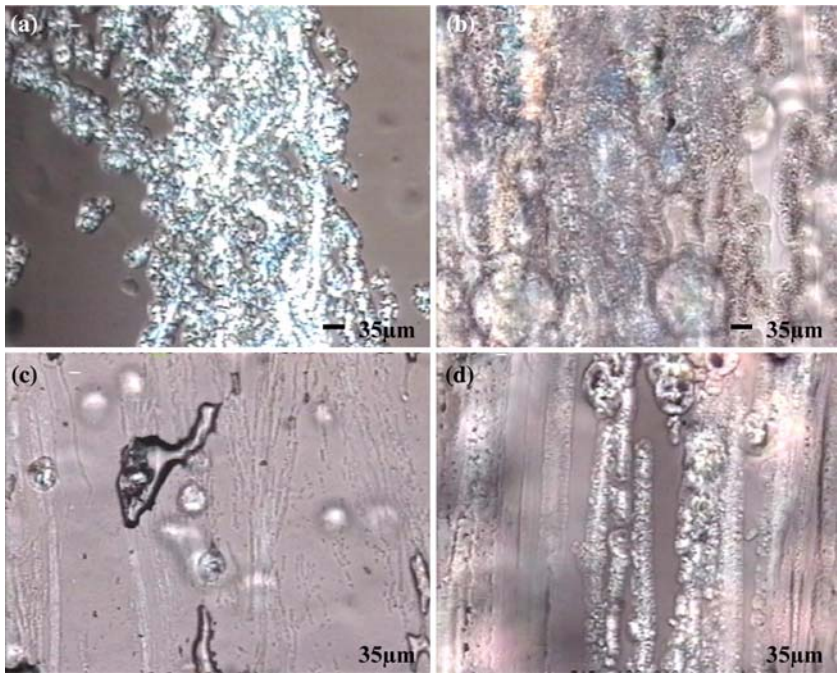

Fig. 2 Rheo-optical micrograph of MMWT/UHMWT PHB (98/2) on the applied shear rate of 100 s^{-1} for 1 s (**a**) at 44 s from the initial shear; (**b**) at 1 min 44 s from the initial shear (different section from (**a**)); (**c**) at the second shear; (**d**) at the fourth shear

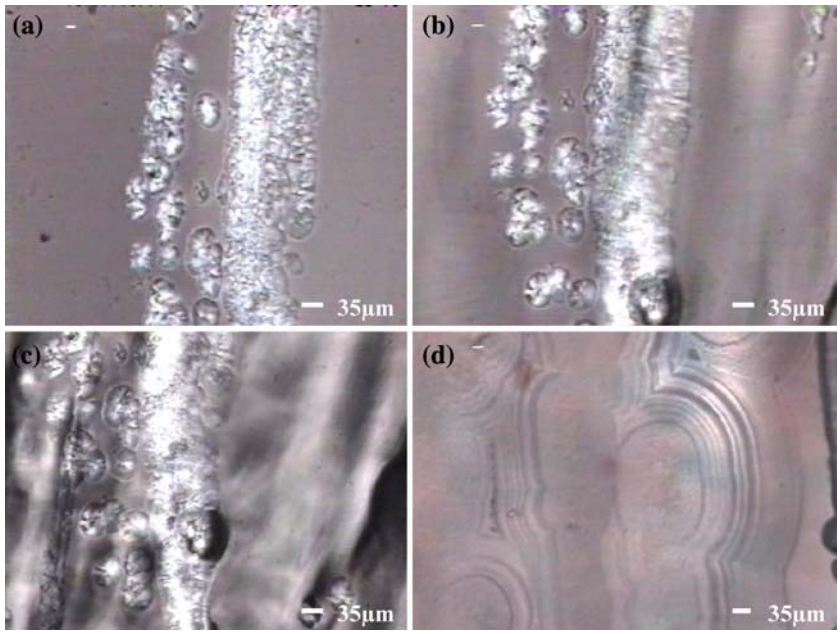

Fig. 3 Rheo-optical micrograph of MMWT/UHMWT PHB (97/3) on the applied shear rate of 100 s^{-1} for 1 s (**a**) at the third shear; (**b**) at the fourth shear; (**c**) at the 5th shear; (**d**) MMWT/UHMWT PHB (98/2) on the applied shear rate of 70 s^{-1} for 1.42 s at the second shear

crack like patterns and a patchwork quilt pattern [8], these findings are a result of the excessive wear and tear that shear produces, Fig. 3d.

The light scattering results identified shish formation as complete (displayed as a line which cuts through the circle) for all compositions analyzed for the initial shears, however on continual shearing the spherulite pattern emerged, Fig. 5. The higher the amount of high molecular weight species present the longer the complete shish remains. Here, the light scattering line was maintained (hold time) with greater thickness and intensity. This has been attributed to the number of shishes formed (line length) and the shish stability (hold time) [7, 8]. However, at MMWT/UHMWT PHB (97/3) the hold time is not long but, an extremely thick and intense shish line results. We propose the higher molecular weight chains add stability to the fibre and the shear condition forces excessive orientated row nuclei, when combined together excessive nucleation and crystallisation rates emerge which result in stable fibre formation and subsequently a stable shish-kebab.

In addition, we notice these fibres remain in view, i.e., attaching to the shear flow glass band during shear application, this indicates excessive stability within

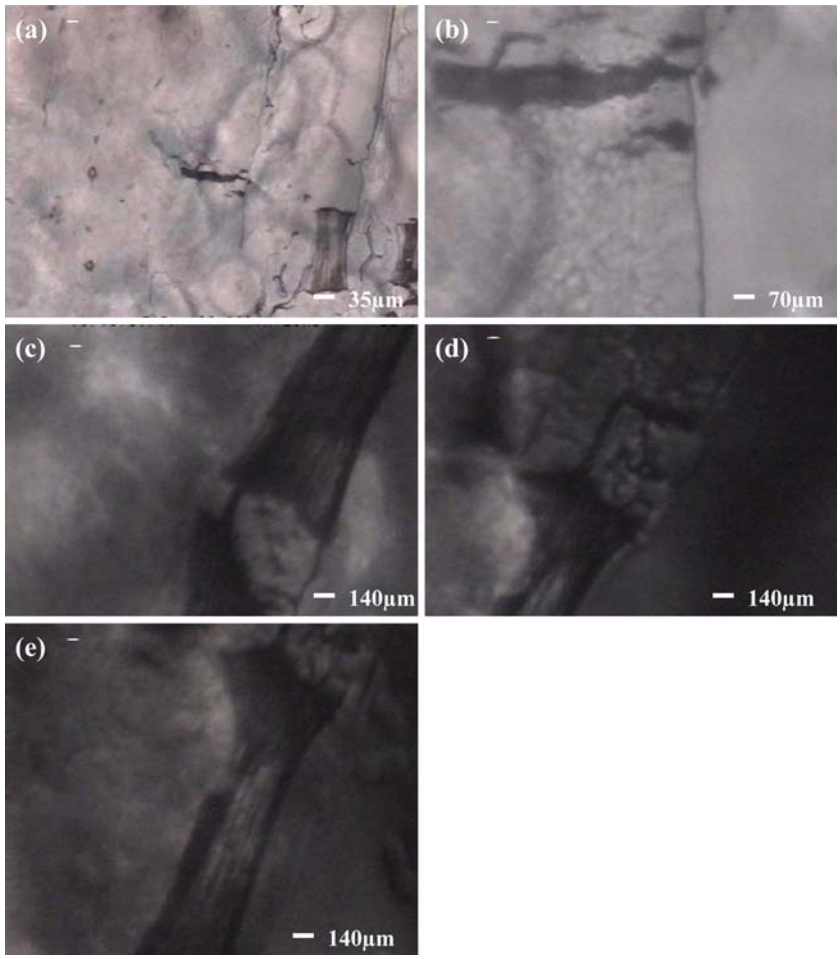

Fig. 4 Rheo-optical micrograph of MMWT/UHMWT PHB (98/2) on the applied shear rate of 35 s^{-1} for 2.85 s (**a**)–(**f**) at the third shear

these units. Previously the strands/orientated structures either became disrupted or were washed away (part of the flow) from view, see Fig 3.

On applying lighter semi continuous shears to the higher ultra high molecular weight blends, after 2 to 3 shears, we were able to shave off the outer layer of the row nucleated structure, Fig. 4. However, what cannot be established is whether this exposed profile is a mass collection of individual shish or the microkebabs, [26–28] (i.e. in this case shaving off the macrokebabs). The latter is likely since the shish is significantly smaller compared to the huge kebabs. On observation, the exposed part appears only slightly smaller to the shaved off unit, the thickness is evident on comparison of the unshaved part. Another possibility though is this shear technique rapidly increases the shish thickness, this could also explain the shishes' extreme stability evident from the light scattering studies previously discussed. Additionally previous researchers have established that strong tie molecules exist between shish and kebabs [29–36] and also between macro and micro kebabs, what we maybe identifying is the destruction of these attachments.

Following these studies, we examined the effect of shear flow on significantly increasing the ultra high molecular weight species using the semi-continuous shear flow method. We noticed a complete difference in morphology compared to the low UHMWT compositions. Instead of observing orientated row nucleation and fibre formation, we actually view disorientated fibres see Fig. 6. This disorientation appears to significantly increase on raising the molecular weight. These unaligned fibres actually curve to such a degree that hook like structures form and branching occurs, see Fig. 7a, b. On increasing the number of shears, the fibres became increasingly orientated to the flow direction compared to the initial shear. We attribute this disorientation to entanglement, first identified by Graessley [37], here deformation is difficult, since adjacent molecules, which interlink, cause the polymer random walk to have severe resistance to free movement between chains. Several researchers [38, 39] have analyzed the effect of polymer structure, i.e., polydispersity and long-chain branching, and concentration on the entanglement spacing and the nature of the entanglement.

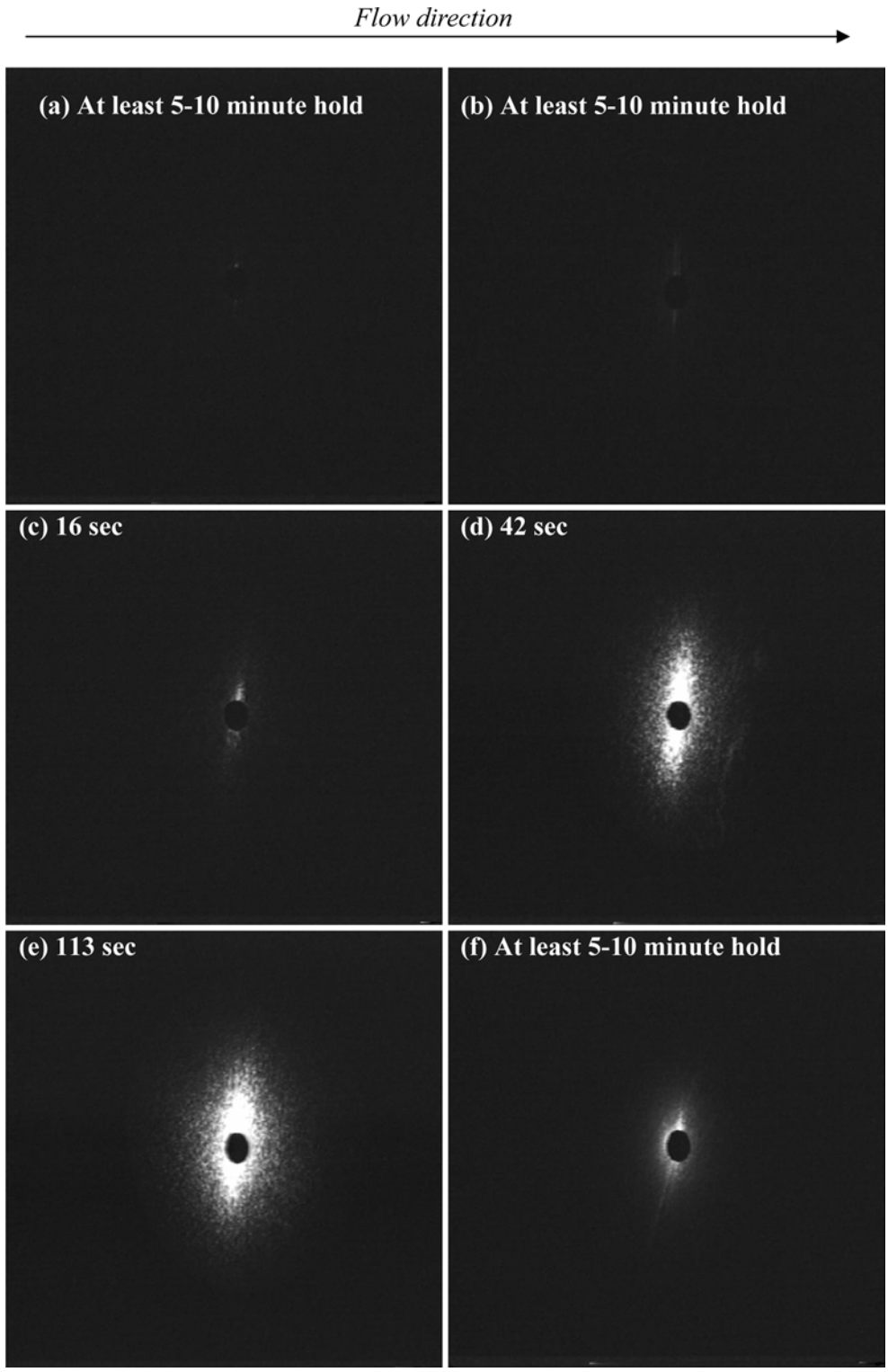

Fig. 5 Rheo-light scattering micrograph on the applied shear rate of 100 s^{-1} for 1 s for (**a**) MMWT/UHMWT PHB (99.5/0.5); (**b**) MMWT/UHMWT PHB (99/1); (**c**)–(**f**) MMWT/UHMWT PHB (98/2); (**g**) MMWT/UHMWT PHB (97/3)

From the light scattering experimentation the partial and complete shish formation is only obtained after a high number of shears, Fig. 8. At MMWT/UHMWT PHB (95/5), (90/10) and (85/15) the shish formed between 10 and 20 shears, for a short period, resulting in spherulite formation. This indicates that under entanglement conditions a stable shish cannot form however, on numerous semi-continuous shearing these chain restrictive entanglements are removed and orientation occurs. This then allows the shish to form, below 10 shears the shish is still trying to exist since we observe an extremely rapid shish during shear.

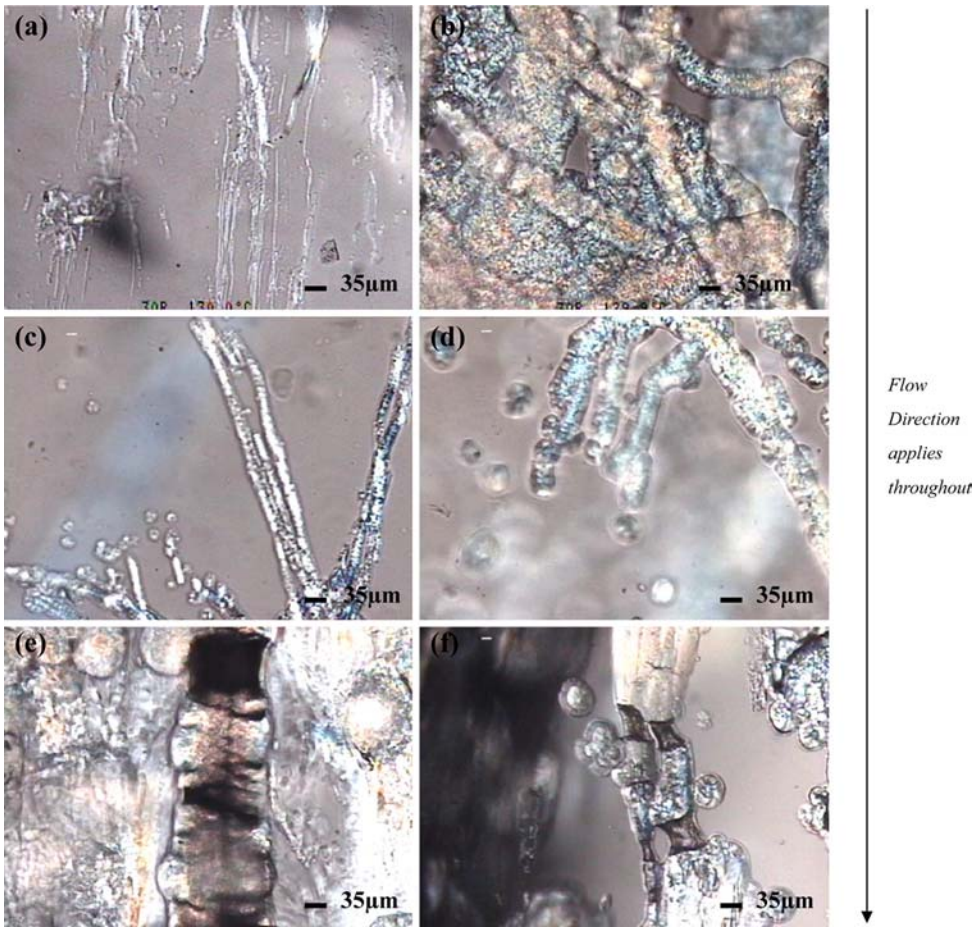

Fig. 6 Rheo-optical micrograph of MMWT/UHMWT PHB (95/5) on the applied shear rate of 100 s^{-1} for 1 s (**a**) at the initial shear; (**b**) at the second shear MMWT/UHMWT PHB (90/10) on the applied shear rate of 100 s^{-1} for 1 s; (**c**) & (**d**) at the initial shear; (**e**) at the second shear; (**f**) at the third shear

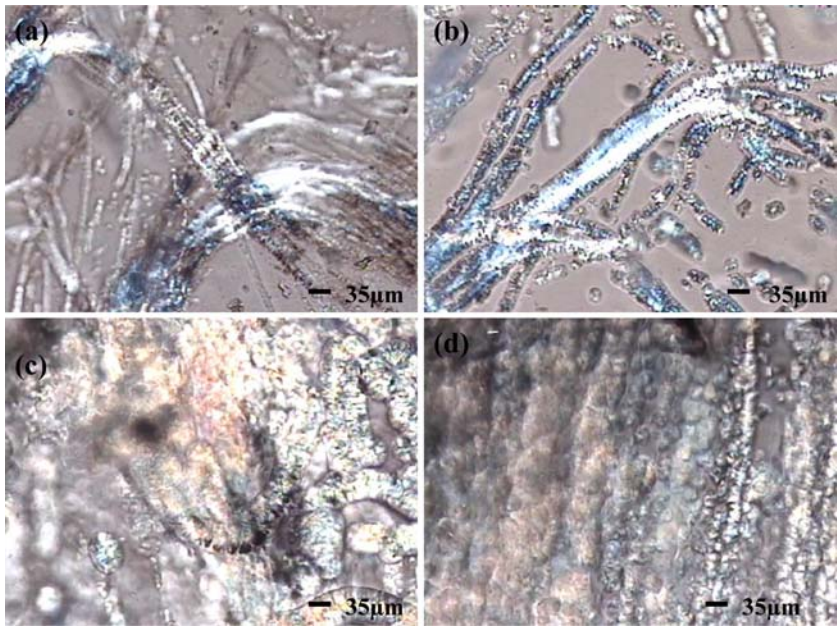

Fig. 7 Rheo-optical micrograph of MMWT/UHMWT PHB (85/15) on the applied shear rate of 100 s^{-1} for 1 s (**a**) & (**b**) at the initial shear; (**c**) at the third shear; (**d**) at the fourth shear

The entanglements observed influence the polymer systems viscosity, thus there exists a critical molecular weight for entanglement formation. For our blends, at initial shears the system acts in the same manner as a cross linked network this becomes more intense, defined as the number of associated entanglements, as the

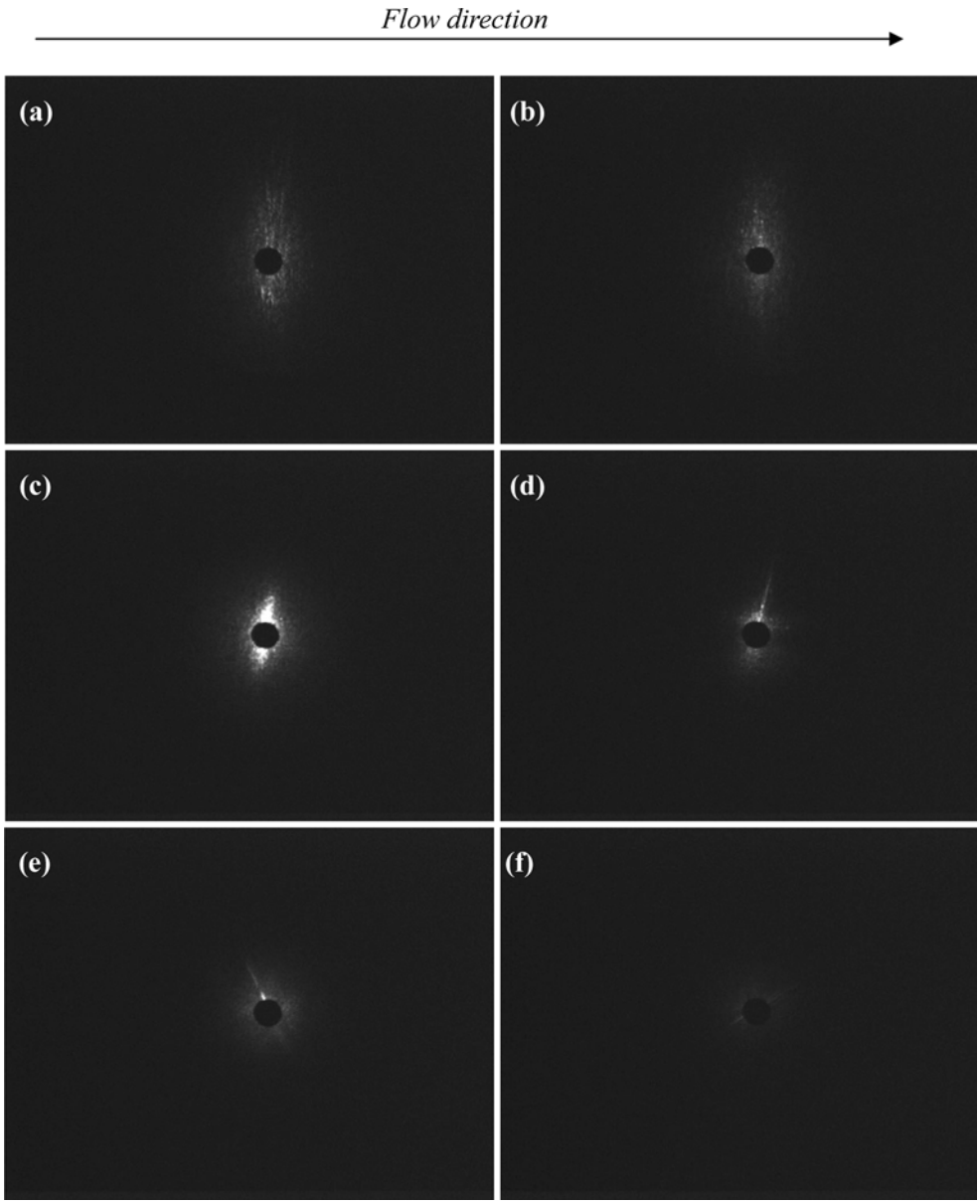

Fig. 8 Rheo-light scattering micrograph between 10 and 20 shears at the applied shear rate of 100 s^{-1} for 1 s for (**a**) & (**b**) MMWT/UHMWT PHB (95/5); (**c**) & (**d**) MMWT/UHMWT PHB (90/10); (**e**) & (**f**) MMWT/UHMWT PHB (85/15)

ultra high molecular weight species is increased. However, on successive high shearing these ''cross links'' or entanglements are removed, this removal is dependent on the number of shears and the molecular weight concentration. We suggest the entanglement critical molecular weight is between MMWT/UHMWT PHB (97/3) and (95/5). These strong intermolecular interactions completely change the systems morphology and this explains our observations.

Interestingly, we also observe stripping of the fibre, Fig. 6, resulting in the exposure of the fibre inner core, this has previously been attributed to the removal of the outer kebabs [8, 26–28].

From these observations, orientated fibres are necessary to produce the optimum shish kebab morphology, using our semi continuous shear method, we believe this is achieved within a narrow molecular weight range MMWT/UHMWT PHB between (98/2) and below (95/5). The entanglement critical molecular weight we propose exists above (97/3) and below (95/5).

Conclusion

In conclusion, the semi-continuous shear method we have developed guarantees fibre formation and excessive stability of the shish in MMWT/UHMWT PHB blends. This enforces the theory that the way shear is applied is crucial to the resultant morphology.

However, we cannot establish the role of the molecular weight with respect to this new method, to substantiate this we are currently, using rheo-methods, to investigate if a stable shish and fibre formation can also be achieved using MMWT/HMWT PHB ($M_w 1 \times 10^6$) blends or if this is only possible in UHMWT blends.

We found that on applying our semi continuous shear flow technique to significantly larger amounts of the ultra high molecular weight species, disorientated fibres occur. We attribute this disorientation to the severe entanglement of the polymer chains acting like cross links, similar to those found in polymer gels. On severe shearing (10–20 shears) the fibres become orientated and the shish formation, both partial and complete is observed. We also expose the inner fibre core we have previously attributed to the possible stripping of the outer kebabs.

Acknowledgements The authors are extremely indebted to and would like to thank JSPS, Japan and The Royal Society, UK for the awarded JSPS fellowship to Dr Lakshmi Sharma.

References

1. Ray AR, Sharma RJ (1995) Macromol Sci Rev Macromol Phys 35:327
2. Doi Y (1990). Microbial polyesters, 1st edn. VCH Publishers, New York
3. De Konig GJM, Lemstra PJ (1992) Polymer 33:3295
4. De Konig GJM, Lemstra PJ (1993) Polymer 34:4089
5. Hay JN, Harris A, Biddlestone F, Hammond T (1996) Polym Int 35:4598
6. Hay JN, Sharma L (2000) Polymer 41: 5749
7. Sharma L, Ogino Y, Kanaya T (2004) Macro Mater Eng 289:1059
8. Sharma L, Ogino Y, Kanaya T, Iwata T, Doi Y (2004) Macrol Mater Eng 289:1068
9. Kumaraswamy G, Issaian AM, Kornfield JA (1999) Macromolecules 22:7537
10. Kumaraswamy G, Varma RK, Issaian AM, Kornfield JA, Yeh F, Hsiao BS (2001) Polymer 41:8931
11. Nogales A, Hsiao BS, Somani RH, Srinivas S, Tsou AH, Balta Calleja FJ, Ezquerra TA (2001) Polymer 42:5247
12. Vleeshouwers S, Hmeijer EH (1996) Rheol Acta 35:391
13. Moitzi J, Skalicky P (1993) Polymer 34:3168
14. Tribout T, Monasse B, Haudin FJ (1996) Colloid Polym Sci 274:197
15. Haudin FJ, Monasse B (1999) J Mater Sci 34:2089
16. Misra S, Lu FM, Spruiell JE, Richeson GC (1995) J Appl Polym Sci 56:1761
17. Sherwood P, Price F, Stein R (1978) J Polym Sci 63:77
18. Lagasse R, Maxwell B (1978) Polym Eng Sci 18:215
19. Wolkowicz M (1978) J Appl Polym Sci 63:365
20. Kusaka S, Abe H, Lee SY, Doi Y (1997) Appl Microbiol Biotechnol 47:140
21. Iwata T, Aoyagi Y, Fujita M, Yamane H, Doi Y, Suzuki Y, Takeuchi A, Uesugi K (2004) Macromol Rapid Commun 25:1100
22. Keller A, Machin MJ (1967) Macromol J Sci Phys Ed (B) 1:41
23. Keller A, Kolnaar WHH (1997) In: Processing of polymers, 1st edn, vol. 18. pp 189–268 (chap. 4)
24. Jerschow P, Janeschitz-Kriegl H (1996) Rheol Acta 35:127
25. Jerschow P, Janeschitz-Kriegl H (1997) Intern Polym Proc 12:72
26. Hill MJ, Barham PJ, Keller A (1980) Colloid Polym Sci 258:1023
27. Hill MJ, Keller A (1981) Colloid Polym Sci 259:335
28. Hill MJ, Barham PJ, Keller A (1983) Colloid Polym Sci 261:721
29. Binsbergen FL, Lange BG (1968) Polymer 9:23
30. Hay JN, Keller A (1967) J Mater Sci 2:538
31. Padden FJ, Keith HD (1966) J Appl Physics 37:4013
32. Padden FJ, Keith HD (1973) J Appl Physics 44:1217
33. Norton DR, Keller A (1985) Polymer 26:704
34. Andersen PG, Carr SH (1975) J Mater Sci 10:870
35. Lovinger AJ (1983) J Polym Sci Polym Phys Ed 21:97
36. Dukovski I, Muthukumar M (2003) J Chem Phys 118:6648
37. Graessley WW (1974) Polym Rheol Adv Polym Sci 16:124
38. Rubinstein M, Colby RH (1988) J Chem Phys 89:5291
39. Colby RH, Rubinstein M, Viovy JL (1992) Macromolecules 25:996