JOURNAL OF MATERIALS SCIENCE **39** (2004) 7373 – 7377 LETTERS

Solvent & second component influence on spherulitic morphology in PHB/PAZO blends

L. SHARMA*, K. NISHIDA, 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

"Polyhydroxybutyrate, (PHB) and poly 1-[4-(3-carboxy-4-hydroxy-phenylazo)benzene sulphonamido-1,2-ethanediyl, sodium salt)], (PAZO), provide a new and exciting range of blend materials, Fig. 1. On harmonization these create the perfect economically viable ecofriendly blend material, with optical data storage and biodegradable ability—a so called "designer photonic material".

The PAZO is an azobenzene derivative containing an N=N bond. This N=N bond is able to cis-trans isomerise, with the isomerisation type dependent on the wavelength of light. The trans type is favorable at 440 nm visible light, whereas the cis type is favorable at 360 nm ultra violet light [1].

PHB is a naturally occurring semi-crystalline biological polymer, forming large banded spherulites when crystallized from the melt, owing to the low nucleation density [2, 3]. Spherulitic studies on PHB blends demonstrate that the second component is initially engulfed in the interlamellar and interfibrillar regions, hindering the lamellar layer process [4–6]. The final spherulitic morphology is then dependent on the second components rejection from these regions, controlled by the interactions arising between the homopolymers.

The area of azobenzene derivative-based blends to produce novel materials is a relatively new research field with only a few papers published [7–9], since achieving miscibility with these highly non-polar groups is extremely difficult. However, we have demonstrated from our previous studies that PHB/PAZO blends are in fact miscible. This is accomplished by solvent blending using acetone, chloroform, and toluene, solvents. We have proposed, using intense DSC and FTIR studies [10, 11], that a complex is formed via a hydrogen bonded "bridge" between the two structures. This "bridge" can only be formed at high PHB composition. Earlier reported calculations have shown PHB/PAZO must be present in a 2–4:1 ratio (dependent on solvent type) for the complex to form. However, nothing is known of this blend morphology and the way in which this complex formation will affect the spherulitic structure. These PHB/PAZO blends have immense potential as a new generation of designer biophotonic materials, but critical to this role is identifying and understanding the PAZO and solvent participation in the resultant morphology. In this paper, by observing the spherulite growth rates we will establish the PHB/PAZO morphology and the underlying interactions of this complex formation.

All chemicals used were purchased from Aldrich Chemicals, Japan. Blends were prepared, by % weight, at PHB/PAZO 20/80, 40/60, 60/40 and 80/20. The selected solvent was added and stirred thoroughly for at least 3 to 6 hrs. The resultant blend remained for over 1 week, ensuring total solvent removal. From previous solubility parameter predictions [10], chloroform is found to be the ideal solvent to establish PHB miscibility. Additionally, blends were prepared in chloroform at PHB/PAZO 90/10, 70/30 and 50/50. Thin film samples were melted on glass cover slips using a hot plate at 180 °C and heated to 200 °C for 2 min and cooled to the desired temperature using Mettler FP90 hot-stage apparatus. Using a video attachment to a Nikon Optiphot 2 Pol microscope, PHB radial growth rates were measured at magnification ×10. For each sample 10–20 readings were observed to obtain an overall growth rate, with at least 5 temperatures per sample measured.

Unfortunately, PHB/PAZO 20/80 spherulitic growth formation proved difficult to observe. The low PHB quantity present and the high PAZO coverage made spherulitic measurement impossible and therefore data was not obtained for this composition.

For all blends, crystallization developed from a small number of spherulites with the characteristic maltese cross and banded birefringence, visible under polarised light. The developing spherulites were extremely large in diameter, several mm in width, owing to PHB's low nucleation density, Fig. 2. The spherulite radius increased linearly with time until the point of impingement by surrounding spherulites. On lowering the PHB content, the spherulitic texture progressively appeared to be coarse with less well defined boundaries amid the spherulites. These observations are consistent with the second component rejection into the interlamellar regions and are in agreement with previous findings [5].

Initial measurement investigated the PHB spherulitic growth rate for each blend condition. For all blends, as expected, the spherulite growth intensifies with the PHB content. The PHB/PAZO 80/20 and 60/40 prepared in chloroform and toluene, Figs 3 and 4, exhibited low growth rates. However, the PHB/PAZO 80/20 and 40/60 prepared in acetone and the latter prepared in toluene revealed sporadic spherulite growth rates, Fig. 5.

---

*Author to whom all correspondence should be addressed.

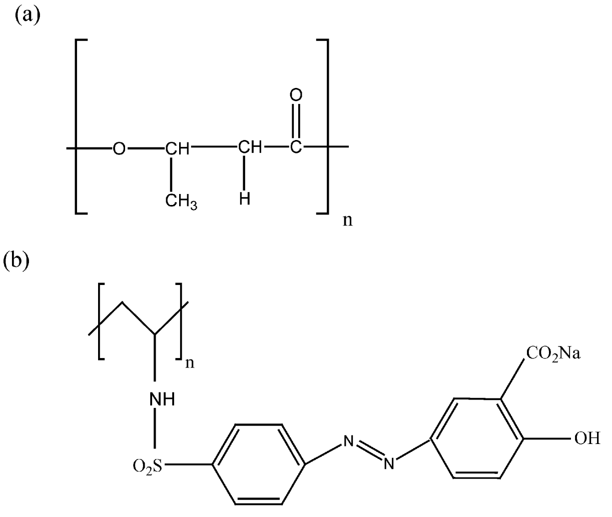

Figure 1 (a) Polyhydroxybutyrate's (PHB) chemical structure and (b) PAZO's chemical structure.

For a specific composition, comparison of the solvents allowed us to determine whether composition dependency was a factor in spherulite growth rate assessment, Figs 6–8. PHB/PAZO 80/20PHB, displayed the greatest spherulitic growth rate in the acetone prepared blend. Chloroform, however, appeared to show only slightly faster spherulite growth rates in comparison to the toluene prepared blends. This trend continues in PHB/PAZO 60/40, where toluene displays a markedly sharp rise in spherulite growth rate, and 40/60, where unexpectedly the toluene displays a faster growth rate than chloroform.

Previous studies have shown a PHB/PAZO complexation exists via hydrogen bonding through the O—H bond at high PHB concentrations. The PHB/PAZO 40/60 observes an extremely high spherulite growth rate. We conclude the occurrence of probable partial complexation, via "bridge" weakening through non-polar interactions, and eventual phase separation, efficient PAZO rejection from the PHB interlamellar and interfibrillar regions.

The PHB/PAZO 80/20, in chloroform and toluene, and the PHB/PAZO 60/40, for all solvents, exhibit low spherulitic growth rates with respect to their blend series. From earlier miscibility studies using DSC and FT-IR [10, 11], we identify that complex formation at these compositions. This indicates, as expected, that complex formation hinders the spherulite growth and is detrimental to the lamellar formation process. One envisages PHB's crystalline front is strongly influenced by the PAZO compared to the solvent, and so hinders the lamellar chain-folding process. In PHB, the crystallographic a-axis is observed to be radial with the b and c rotating around the radius [15]. This rotation occurs by lamellae twisting, producing the characteristic banded appearance and is associated with radially orientated lamellar ribbon elastic bending. If this lamellae twisting is affected by a second component then the spherulitic growth rate will be significantly decreased.

The spherulite growth rates for PHB/PAZO 40/60 are not comparable to the PHB/PAZO 90/10 prepared in chloroform, which leads to the conclusion that complete rejection may not exist. These observations are in agreement with previous studies on PHB/PAZO blends [10, 11].

Focusing on the solvent impact, acetone exhibited the fastest spherulite growth rate. However, in certain cases, this appeared rather sporadic, indicating the lamellar folding process is randomly affected by the PAZO and acetone solvent interactions, which influence the PHB/PAZO complex formation. In PHB/PAZO 80/20 and 60/40, the overall spherulite growth rate increases in the chloroform, compared to the toluene prepared blends. This situation is reversed however, when we observe the PHB/PAZO 40/60 blends deducing that the spherulite growth rate in the acetone solvent is

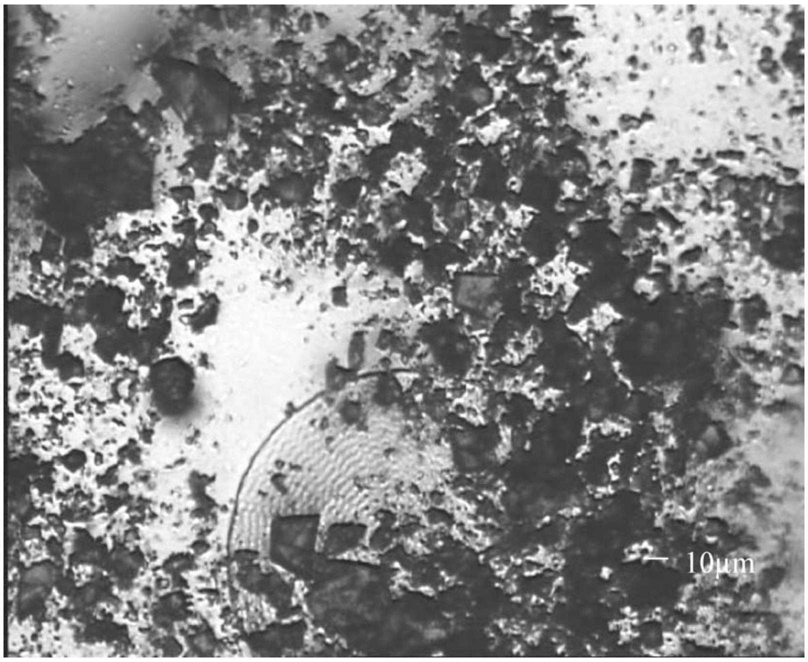

Figure 2 Optical microscope photograph of 40/60 PHB/PAZO in chloroform solvent at 64 °C.

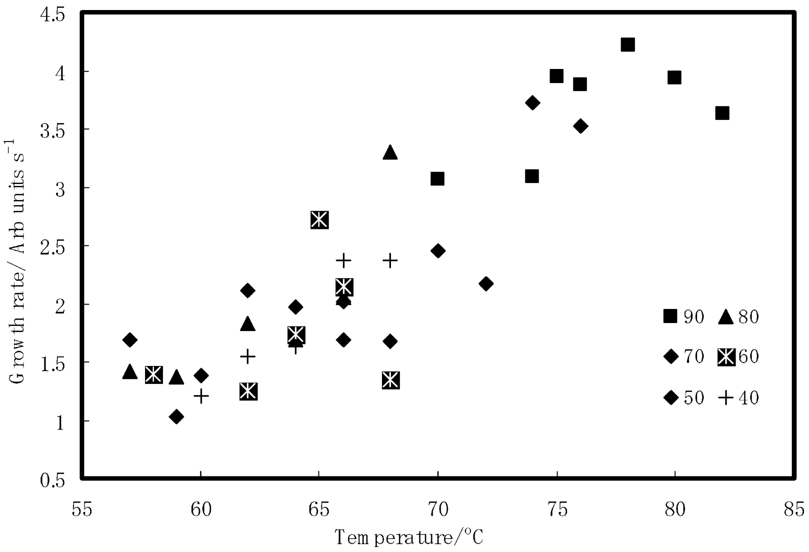

Figure 3 The spherulite growth rate of PHB/PAZO blends prepared in chloroform.

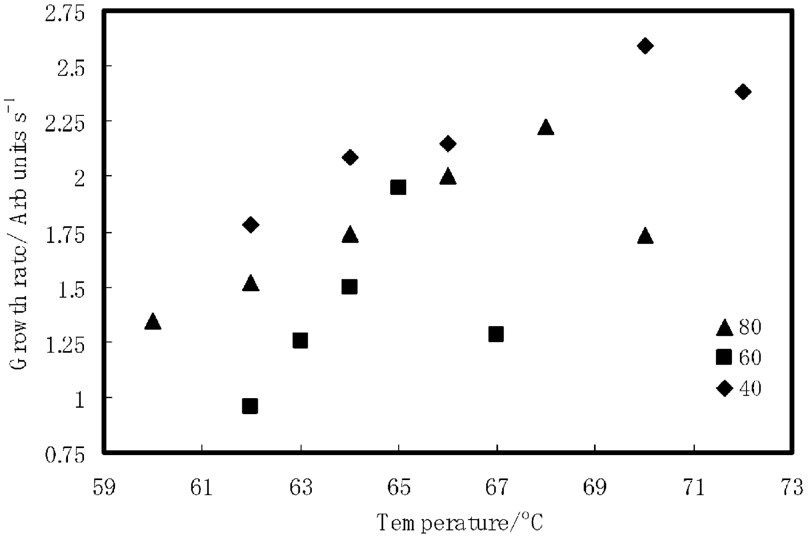

Figure 4 The spherulite growth rate of PHB/PAZO blends prepared in toluene.

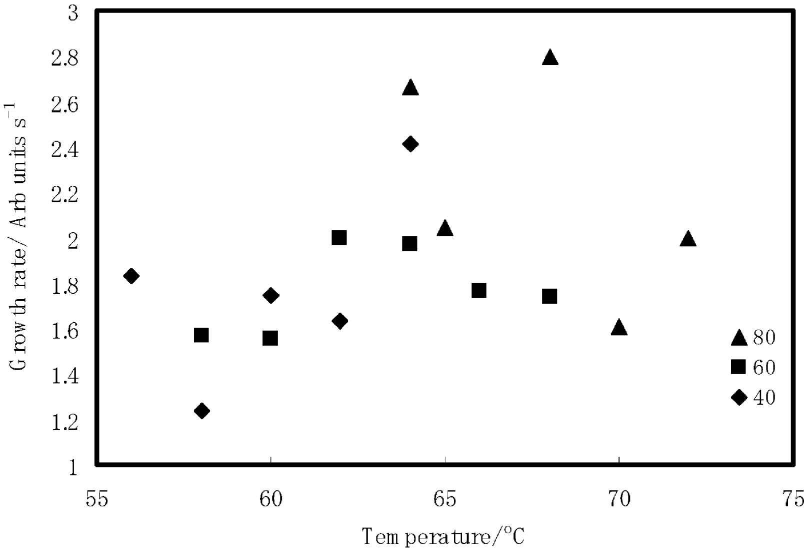

Figure 5 The spherulite growth rate of PHB/PAZO blends prepared in acetone.

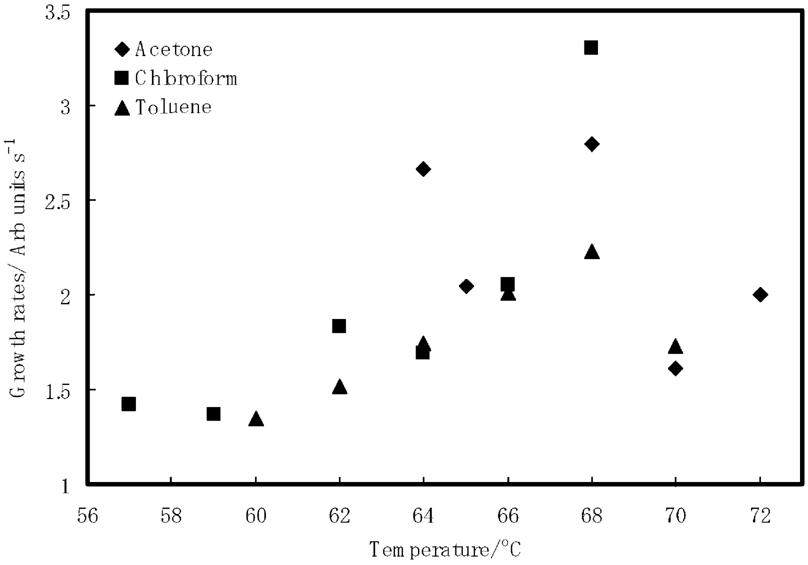

Figure 6 The spherulitic growth rate at PHB/PAZO 80/20 for all solvents.

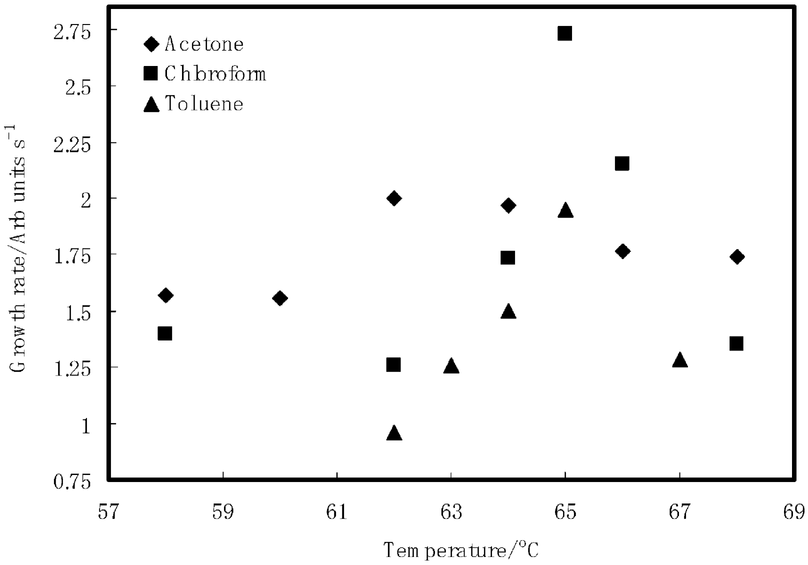

Figure 7 The spherulitic growth rate at PHB/PAZO 60/40 for all solvents.

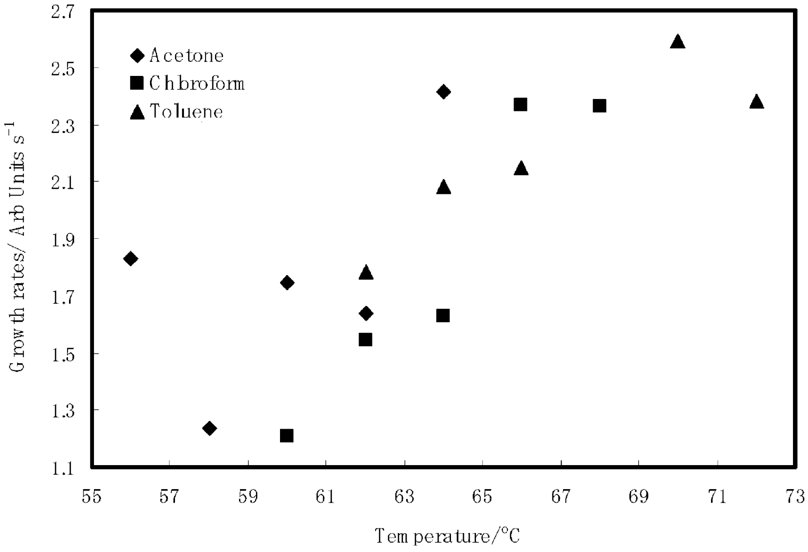

Figure 8 The spherulitic growth rate at PHB/PAZO 40/60 for all solvents.

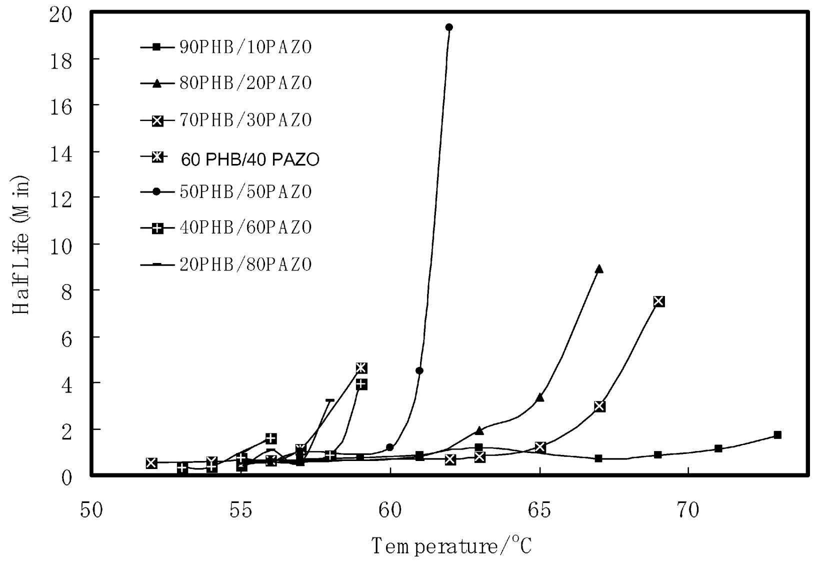

Figure 9 The hot isothermal crystallizations (half-life's) for PHB/PAZO blends prepared in chloroform.

composition independent, but dependent on the chloroform and toluene solvents.

Hot isothermal crystallizations in the chloroform prepared blends were studied to further substantiate this paper's findings, Fig. 9. Using a Perkin Elmer Series 7 differential scanning calorimeter, blend samples, 10–15 mg, were initially heated to 200 °C and annealed for 2.5 min, thus removing any previous thermal history. After this annealing, the sample was immediately cooled to the desired crystallization temperature. At least two runs per sample were measured to ensure good reproducibility and consistency of results. The DSC was calibrated using indium, melting point 429.8 K and heat of fusion 28.4 Jg^{-1}. The blends displayed increasing crystallization rates with PHB composition. In agreement with the spherulite growth rates previously mentioned, the PHB/PAZO 80/20 and 60/40 exhibited a low crystallization rate. However, contrary to these same studies, the PHB/PAZO 40/60 showed no signs of faster spherulite growth rates arising from measurement at low or hot temperatures. This experimentation is in agreement with the DSC, FT-IR, and microscope studies confirming a PHB/PAZO complex exists at high PHB compositions.

Acknowledgments

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. S. TRIPATHY and D. Y. KIM, "Photonic and Optoelectronic Polymers" (American Chemical Society-ACS Symposium Series, 1997) vol. 672, p. 67.
2. Y. DOI, "Microbial Polyesters" (VCH Publishers, New York, 1990).
3. R. J. SHARMA and T. ASANO, *Macromol. Sci.-Rev. Macromol. and Phys.* **35** (1995) 327.
4. C. LAUZIER, R. H. MARCHESSAULT, P. SMITH and H. CANZY, *Polymer* **33** (1992) 823.
5. L. SHARMA, Ph.D. Thesis, Birmingham University, UK, 1998.
6. J. N. HAY and L. SHARMA, *Polymer* **41** (2000) 5749.
7. L. SHARMA, T. KIMURA and H. MATSUDA, *Polym. Adv. Technol.* **13** (2002) 450.
8. L. SHARMA and T. KIMURA, *ibid.* **14** (2003) 1.
9. S. XIE, A. NATANSOHN and P. ROCHON, *Macromolecules* **27** (1994) 1489.
10. L. SHARMA, K. NISHIDA and T. KANAYA, *submitted.*
11. *Idem. submitted.*
12. A. J. OWEN, *Polymer* **38** (1997) 3705.

Received 12 March
and accepted 3 June 2004