

Study of the Dispersion of Low-Density Polyethylene Additive Masterbatches in Polyolefins

O. OGBOBE*

Institute of Polymer Technology, Loughborough University of Technology, Loughborough, LE 11 3 TU, England

SYNOPSIS

Light microscopy, X-ray microradiography, and ultraviolet microscopy have been used to examine pigment dispersion in low-density polyethylene pigment masterbatches and polyolefin/low-density polyethylene additive masterbatch extrudates. The results obtained show that the dispersions of pigment additives in the low-density polyethylene masterbatches studied were very poor. Also, the degree of dispersion of low-density polyethylene pigment and ultraviolet masterbatches depend on the melt-flow-index of high-density polyethylene. Blend is poor because of the two-phase nature of the mix. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Homogeneously dispersing additives into polymers at a concentration of about 0.5–2% by a masterbatch technique has become one of the preferred ways of incorporating additives into polymers for whatever reason, be it imparting of color, protection against ultraviolet (UV) light, or the prevention of two polyolefin film surfaces from sticking together without making the surface slippery.

Gilroy and Howard¹ demonstrated that the color strength, UV protective action, etc., given to a base polymer containing additives is realized fully only if the additive dispersion quality is reasonably good. A reasonable level of dispersion and distribution depend on the application for which the product is designed; for instance, pigment particle sizes of 50 μm and above may create an associated problem of stress concentration, whereas a pigment size of up to 5 μm can influence the electrical properties of a fabricated product. A reasonable level of dispersion of pigment in a product for electrical application should therefore be less than 5 μm . The most convenient and accurate method of pigment dispersion measurement in plastics is by the viewing of melt-

pressed or microtomed samples under an optical microscope.^{2,3} This procedure is tedious and subjective. The valuable work of Endter and Gebauer⁴ that used a semi-automatic device for the study of particle-size distribution in a microscope photomicrograph has largely removed the subjectivity associated with the optical microscope method. Burgess et al.⁵ and Hess⁶ also reported more practical image analyzers based on feature-specific image analyzes utilizing a Quantiment 720 system with a television camera linked to a TEM by a fiber optic coupling. Surface roughness variation in rubbers brought about by varying carbon black dispersion levels and microdensitometric methods have also been used by Vegvari et al.⁷ and Best and Tomfotirde,⁸ respectively, for the quantitative measurement of carbon black dispersion.

Reported work on the application of these characterization methods to polyolefins where low-density polyethylene (LDPE) has been used as a means of incorporating additives is very scanty. Martin⁹ used a qualitative assessment procedure to point out the problem created by blending the masterbatch and the natural polymer to the degree of pigment dispersion. Gale¹⁰ showed that a single pass of polyethylene and the LDPE masterbatch in a single-screw extruder results in the masterbatch existing as thin laminar streaks separated by layers of unpigmented natural polymer. He reported that subsequent examination of such extrudates gave rise to additive striations originating from the melting of

* Present address: Department of Polymer & Textile Technology, School of Engineering and Engineering Technology, Federal University of Technology, P.M.B. 1526, Owerri, Imo State, Nigeria.

individual masterbatches. A mixing device that divides shearing with a repeated cutting and turning action has been suggested for producing polyolefin extrudates from blends of natural polyolefin and LDPE carbon black masterbatches^{10,11} that meet the British standards dispersion requirements.

Much remains to be understood on the subject of use of LDPE masterbatches on overall dispersion in polyolefin/masterbatch extrudates. For instance,

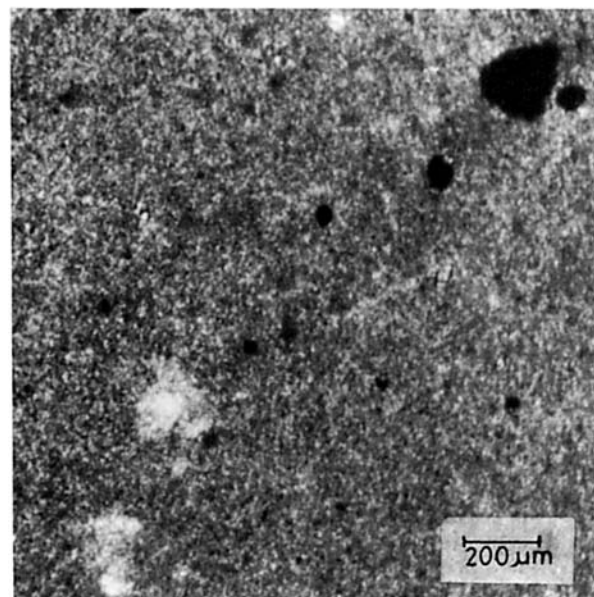
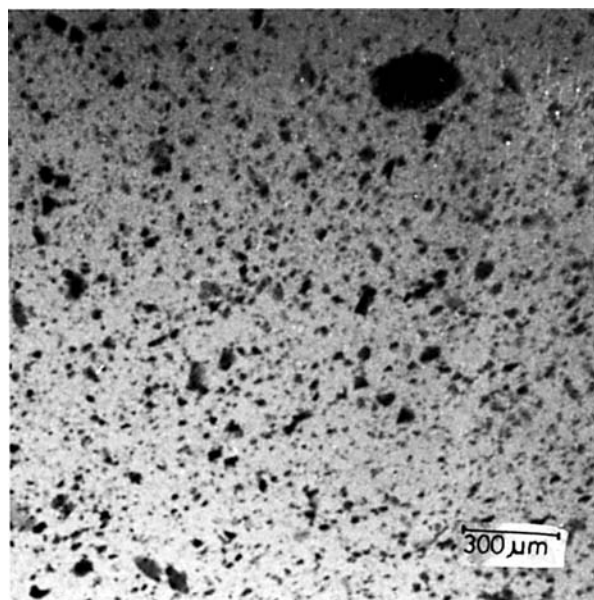


Figure 1 (a) X-ray microradiograph of LDPE masterbatch. (b) Transmitted light micrograph of the specimen shown in (a).

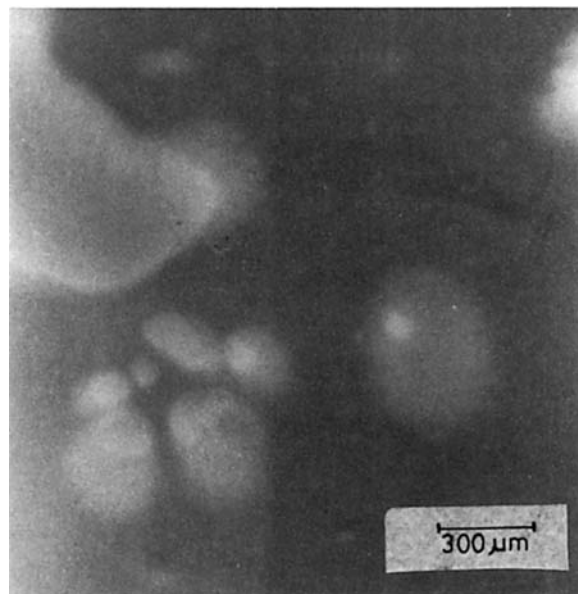


Figure 2 Transmitted light micrograph of an all-organic LDPE pigment masterbatch.

only a few additive carriers are commercially available compared to the large range of polyolefins of varying melt-flow-index (MFI). The use of LDPE masterbatches with polyolefins without regard for varying molecular structure may lead to dispersion problems, as it is known that polymers of diverse molecular weight do not mix.¹² In this work, the uniformity of additive dispersion in LDPE masterbatches was initially examined by X-ray microradiography and optical microscopy to ensure that any inferior additive dispersion in the extrudates was not caused by poor additive dispersion in the masterbatches employed. Following a single-screw extrusion of masterbatches and natural polyolefin, the quality of additive dispersion in polyolefin/LDPE extrudates was examined by light microscopy for pigmented extrudates and UV microscopy for polyolefin/UV absorber extrudates. The degree of miscibility of polyolefins and LDPE were assessed by scanning electron microscopy (SEM) after solvent etching in hot xylene and differential thermal analysis (DTA).

EXPERIMENTAL

(a) Materials

The following polymers and masterbatches supplied by Cole Plastics, Bramley Road, Milton Keynes, were used in the present study:

Polyolefins: High-density polyethylene (HDPE) (rigidex 002-55, MFI = 0.2; rigidex HO-6045 P(2), MFI = 6.0) and polypropylene (PP) copolymer (HSE 110).

LDPE masterbatches: VBM 301 olive drab 22830/3% with composition β : copper phthalocyanine (1.645%), carbon black (0.189%), ferric oxide (5.51%), and a mixture of cad-

mium sulfide, barium sulfate, and zinc sulfide (6.292%).

Pantanone: code VBM 301-22360/3% (undisclosed composition); brown: code VBM 201-22381/3% (undisclosed composition); dark blue: code VBM 301-22363/3% (undisclosed composition); Cyasorb 531: code VBM 301-10,000/1.3% UV and benzidine yellow (an all

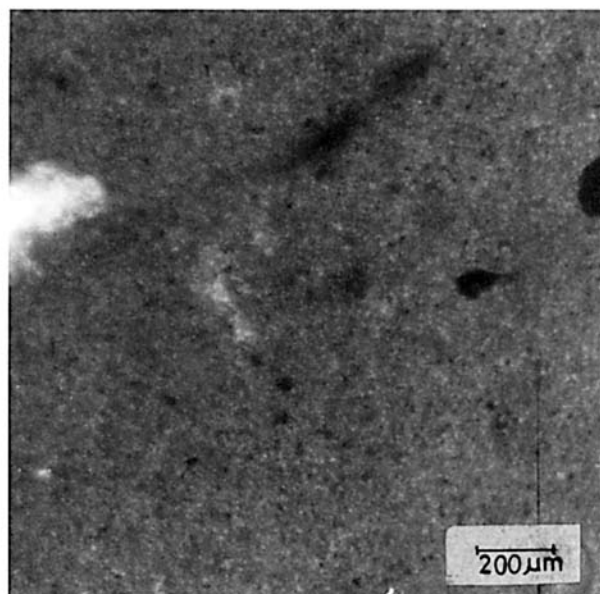
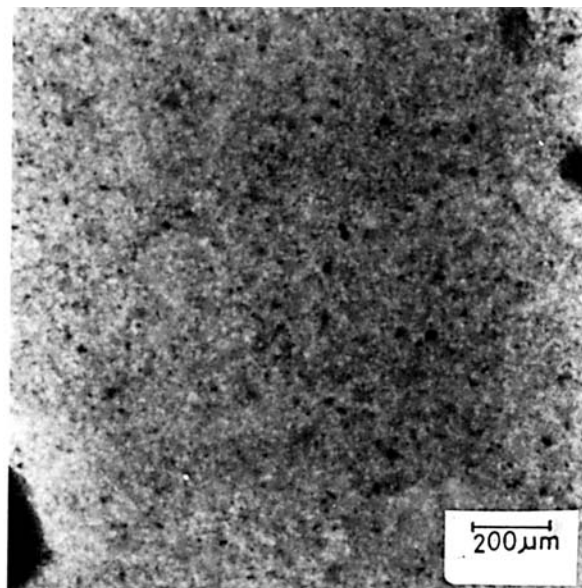
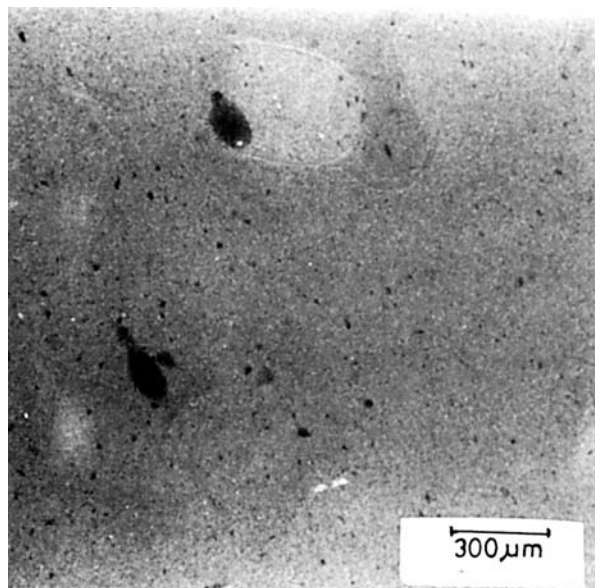


Figure 3 (a) X-ray microradiograph of a Pantanogreen LDPE masterbatch. (b) Transmitted light micrograph of a brown-colored LDPE pigment masterbatch. (c) Transmitted light micrograph of a blue-colored LDPE pigment masterbatch.

organic masterbatch) supplied by D. A. Hem-
sley, IPT, Loughborough.

(b) Characteristics of Dispersion in Masterbatches

Characterization of additive dispersion in master-
batches was carried out by X-ray microradiography
and light microscopy. Although thin sectioning fol-

lowed by light microscopy is well established for ex-
amining the internal morphology of additive-con-
taining materials, the method does not always apply
to materials such as masterbatches with high
amounts of additives.

For this reason, sample preparation for X-ray
microradiography and light microscopy were done
by melt pressing at 160°C between a glass slide and
coverslip on a hot plate. Sample specimens of about

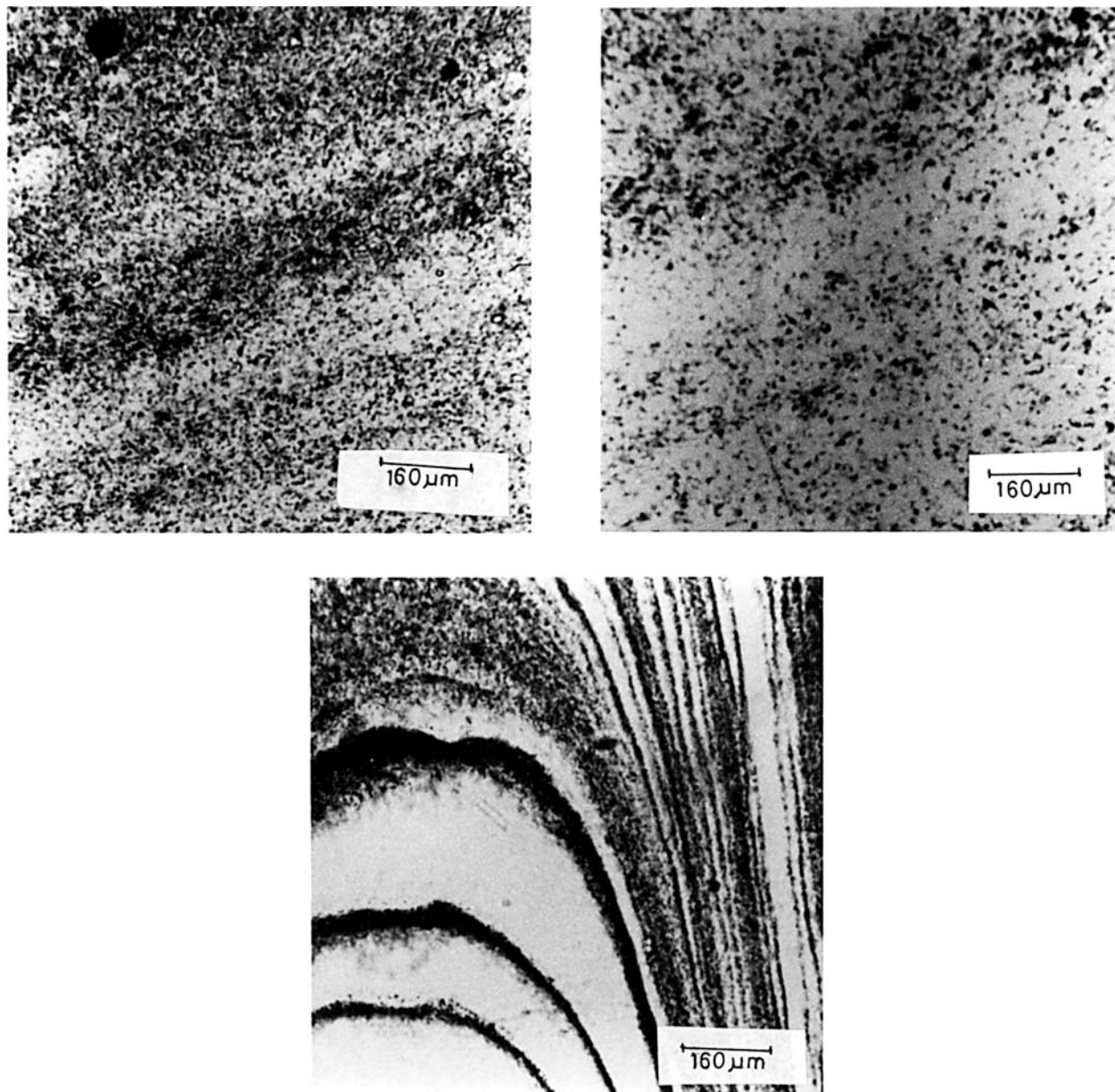


Figure 4 (a) Transmitted light micrograph of a 0.2 MFI HDPE/pigment masterbatch blend. (b) Transmitted light micrograph of a 6.0 MFI HDPE/pigment masterbatch blend. (c) Transmitted light micrograph of PP/pigment masterbatch blend.

50 μm thick were used for X-ray microradiography, whereas very small masterbatch samples were employed before specimens thin enough to allow light microscopy were obtained. The technique of X-ray microradiography is well established.¹³ The procedure used here involves carrying the specimen on a slide-in dovetailed plate and exposing it to X-ray generated from a 4 μm -thick target copper foil bombarded by electrons. X-rays generated in the target and passing through the specimen were recorded by

a 1 cm-square silicon solar cell. The X-ray film is a light tight satchel constructed by sandwiching a photographic film (a Kodak Industrex MX) between black opaque polyethylene film and an opaque adhesive-coated PVC tape. Film was developed in a Kodak DX80 developer for 4 min. The optical light microscopical examination of pigment distribution in the masterbatches was done under a Zeiss light microscope. Transmitted light microscopy was employed in addition to X-ray microradiography to be

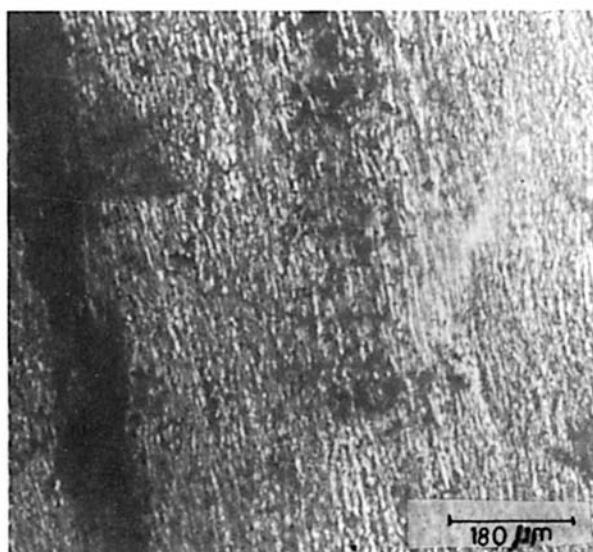
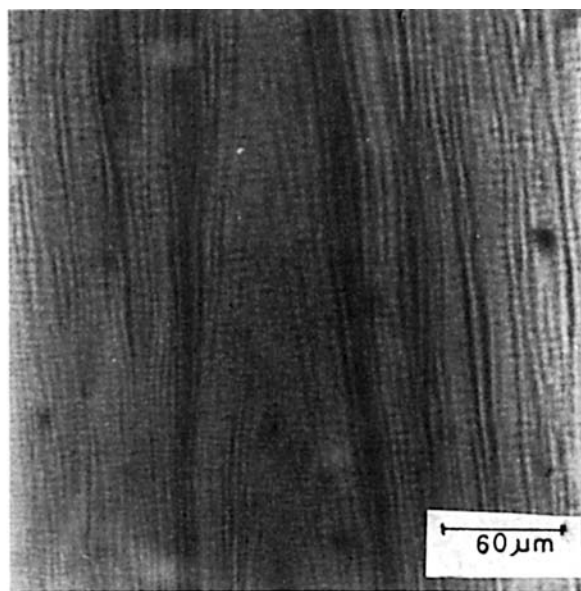
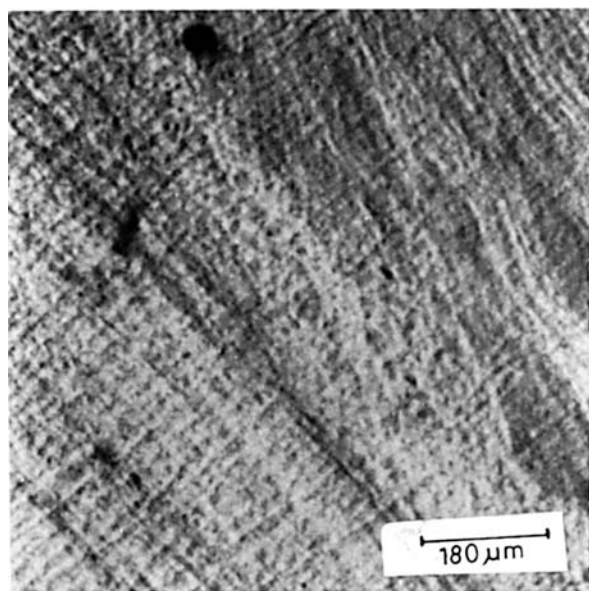


Figure 5 (a) UV micrograph of 6.0 MFI HDPE/LDPE UV masterbatch. (b) UV micrograph of 0.2 MFI HDPE/LDPE UV masterbatch. (c) UV micrograph of PP/LDPE UV masterbatch.

able to discriminate between the dispersibility of inorganic and organic components in the masterbatches.

(c) Preparation of Extrudates and Extrudate Sections

To investigate the effect of molecular weight on the degree of dispersion, polyolefin/masterbatch blends were, respectively, extruded for each of rigidex 002-55, BP MFI = 0.2; rigidex HO-6045 P(2), MFI = 6.0 (HDPEs); and PP copolymer with each of VBM 301-22380/3% and VBM 301-10,000/1.3% (cyasorb 531). A 1 in.-type laboratory extruder (Model CS-194, manufactured by Instron Scientific Instruments Inc.) using a 20 : 1 polyethylene screw was used. The extrusion was done between 140 and 160°C and at die temperature of 170°C/screw speed of 10 rpm for 6.0 MFI HDPE; between 150 and 180°C and at die temperature 190°C/rpm for 0.2 MFI HDPE; and between 170 and 200°C and at die temperature of 210°C/10 rpm for PP to give a 1% pigment content and 0.5% UV absorber content.

For examination of the pigment and UV absorber-containing extrudates, thin sections (10 μm thickness for pigmented specimens and 5 μm thickness for UV absorber-containing specimens) were cut across the extrusion direction using a Leitz 1400 microtome with a D profile blade. Since a major problem in UV microscopy is diffraction effects that occur at the surfaces when poor sectioning gives rise to a rough surface, extra care was taken to avoid rough sample surfaces. The sections were mounted between a standard slide (quartz slide/coverslip for UV work) and coverslip in an appropriate immersion oil (non-UV-absorbing immersion oil was employed for specimens containing UV absorbers).

Dispersion of pigment in the extrudates was studied by a Zeiss light microscope equipment, whereas UV-absorber dispersion was investigated using a custom-built microscope equipment, consisting of an Ernst Leitz microscope stand equipped with Zeiss quartz optics, a 500 W high-pressure mercury vapor lamp (150 atm), a monochromator, an image converter, and an Olympus 0M1 camera.¹⁴

RESULTS AND DISCUSSION

Masterbatch Studies

When sections of additive-containing plastics are examined by X-ray microradiography, only the high atomic number inorganic elements distributed in the

transparent polymer matrix are visible. For transmitted light microscopy, both the organic and inorganic components of the additives are visible. Our studies on additives in LDPE masterbatches using X-ray microradiography and transmitted light microscopy have shown that the degree of dispersion of pigments in the LDPE masterbatches used in this study is poorly generated. Figure 1 (a) and (b) compare the X-ray microradiography and transmitted light micrograph of VBM 301-22380/3%. In line with the observation of Ahmed¹⁵ that carbon black and iron oxide are among the most difficult pigments to disperse in a polymer matrix, poorer dispersion was found in the masterbatch VBM 301-22380/3%, which contains 5.51% iron oxide, 1.645% β -copper phthalocyanine, and 6.292% of a mixture of barium sulfate, zinc sulfide, and cadmium sulfide.

Figure 2 is a transmitted light micrograph of a yellow masterbatch containing benzidine yellow, which is known to make impossible the heat sealing of polyethylene bags containing it.¹⁶ The dispersion of the pigment in the LDPE matrix is extremely poor. Figure 3(a), pantanone green; (b), brown masterbatch; and (c), dark blue masterbatch, are some of the other pigment masterbatches studied. Figure 3(a) is an X-ray microradiography showing poor pigment dispersion, whereas Figure 3(b) and (c) are transmitted light micrographs showing poor dispersion in the former and a fair amount of dispersion in the latter.

Extrudate Studies

Figure 4 shows micrographs of extrudates of 0.2 MFI HDPE, 6.0 MFI HDPE, and PP copolymer, respec-

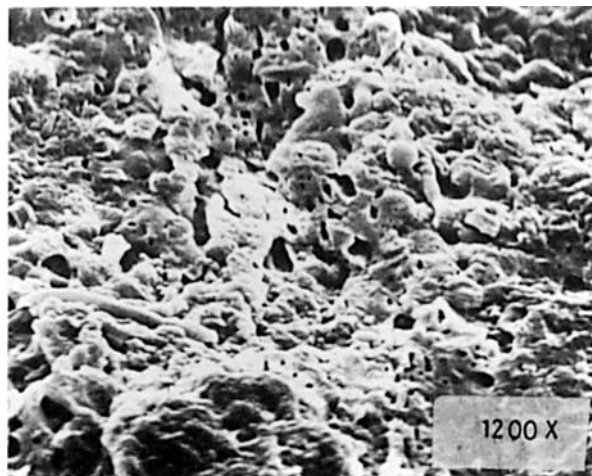


Figure 6 Scanning electron micrograph of etched PP/pigment masterbatch.

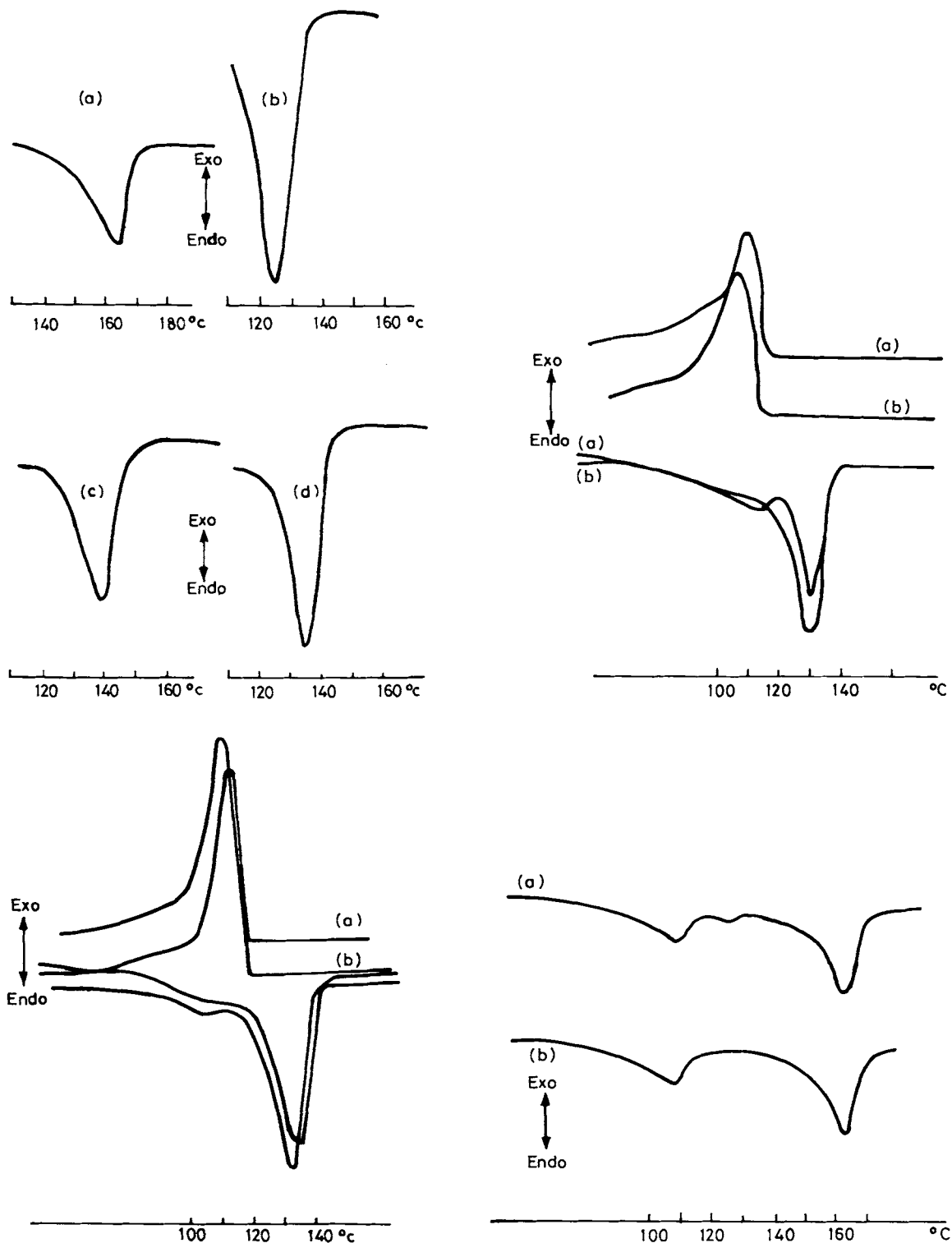


Figure 7 (A) Thermograms of masterbatch and base polymers: (a) polypropylene; (b) masterbatch; (c) 0.2 MFI HDPE; (d) 6.0 MFI HDPE. (B) Thermograms of extrudates of 6.0 MFI HDPE: (a) die temperature 170°C, screw speed 40 rpm; (b) die temperature 170°C, screw speed 10 rpm. (C) Thermograms of extrudates of 0.2 MFI HDPE: (a) die temperature 190°C, screw speed 10 rpm; (b) die temperature 190°C, screw speed 40 rpm. (D) Thermograms of PP extrudates: (a) die temperature 210°C, screw speed 10 rpm; (b) die temperature 210°C, screw speed 40 rpm.

tively, pigmented with the masterbatch VBM 301-22380/3% and processed between 140 and 160°C (die temperature 170°C/screw speed 10 rpm), between 150 and 180°C (die temperature 190°C/10 rpm), and between 170 and 200°C (die temperature 210°C/10 rpm), respectively. The PP extrudate [Fig. 4(c)] shows a very poor distribution of the pigment masterbatch. The 0.2 MFI extrudate [Fig. 4(b)] shows a better pigment dispersion compared to the PP extrudate. Pigment dispersion and distribution is best in the 6.0 MFI HDPE extrudate. The differences in results are considered to have originated from the differences in the molecular weights of the polyolefins and LDPE masterbatch base.

Figure 5 shows a UV micrograph of extrudates of 6.0 MFI HDPE (a), 0.2 MFI HDPE (b), and PP copolymer (c) containing an LDPE-based UV masterbatch. The dark areas show where the UV absorbers are positioned, whereas the light areas indicate parts of the polymer matrix not containing much UV absorber. For this material to be adequately protected from UV light, the whole area should have been uniformly dark. Comparison of Figures 4(a) and (b) and 5(a) and (b) shows that additive dispersion became poorer with a decrease in polyolefin MFI for both pigment and UV absorber. This suggests that a large variation in molecular weight difference between the masterbatch base and base polymer is the origin of the differences in additive dispersion/distribution that have been observed.

Figure 6 is a scanning electron micrograph of a PP/LDPE masterbatch (VBM 301-22380/3%) extrudate etched in hot xylene for 30 min. The micrograph contain voids believed to have been left after a differential attack of solvent on LDPE. The significance of this observation is that the LDPE is present in the PP extrudate as a separate phase. This explains further the very poor additive dispersion observed in this extrudate.

Figure 7 compares the DTA results of the masterbatch, PP, 0.2 MFI HDPE, 6.0 MFI HDPE, and 6.0 MFI HDPE/masterbatch extrudates (die temperatures 170°C/10 rpm and 170°C/40 rpm), 0.2 MFI HDPE/masterbatch extrudates (die temperatures 190°C/10 rpm and 190°C/40 rpm), and PP/masterbatch extrudates (die temperatures 210°C/10 rpm and 210°C/40 rpm). Although solvent-etched samples of the polyethylene blends did not indicate incompatibility, DTA results clearly show that LDPE exists as a separate phase in all the polyolefins used in this study. This is shown by the well-defined crystalline melting point peaks, particularly

at low-temperature/low-shear processing regimes. The melting point peaks of the masterbatch/polyolefins in the extrudates [Fig. 7(B)-(D)] are comparable to the melting points of the virgin polymers [Fig. 7(A)]. At high-temperature/high-shear regimes, compatibility increases. For PP/LDPE extrudates, both PP and LDPE stay as separate phases at the two processing conditions.

CONCLUSIONS

Various methods have been considered for assessing the degree of dispersion of additives in LDPE masterbatches and polyolefin extrudates. Initial examination of additive dispersion in masterbatches was considered necessary to ensure that any inferior dispersions in the extrudates were not caused by poor dispersion in the masterbatch in the first place.

X-ray microradiography and light microscopy have shown that the dispersion of the pigments in the LDPE masterbatches used in this study, particularly those containing iron oxide, barium sulfate, calcium sulfide, and zinc sulfide, are invariably bad. The inferior additive dispersion observed in some polyolefin extrudates may have been partly due to the poor dispersion in the masterbatch.

Transmitted light and UV microscopy showed that the degree of dispersion of the LDPE masterbatch decreased with decrease in polyolefin MFI. This arises because the difference in molecular weight of the masterbatch and the polyolefin widens with decrease in polyolefin MFI.

DTA and SEM have both shown that the LDPE masterbatch stayed as a separate phase in each of the extrudates. The LDPE therefore stayed as streaks in the polyolefin extrudates, causing a greater part of the additive to remain in the streaks. This was very pronounced in low MFI polyolefin/LDPE extrudates.

I wish to acknowledge Cole Plastics, Bramely Road, Milton Keynes, London, for supplying the polymers and masterbatches used in this work. Thanks are due to D. A. Hemsley of Loughborough University of Technology for his advice. Finally, thanks also go to the Federal Government of Nigeria for providing the financial assistance at Loughborough University of Technology, Loughborough, where this work was carried out.

REFERENCES

1. H. M. Gilroy and J. B. Howard, *Polym. Eng. Sci.*, **9**(4), 286 (1969).

2. British Standard 1972: 1967 (Polyethylene pipe type 32 for cold water services).
3. *Masterbatches for Plastics*, Cabot Carbon Ltd. Dun-kinfield, U.K.
4. F. Endter and H. Gebauer, *Optik*, **13**, 97 (1956).
5. K. A. Burgess, C. E. Scott, and W. M. Hess, *Rubber Chem. Technol.*, **44**, 30 (1971).
6. W. M. Hess, ASTM (1974), STP-552.
7. P. C. Vegvari, W. M. Hess, and V. E. Chiroc, *Rubber Chem. Technol.*, **51**, 817 (1978).
8. W. G. Best and H. F. Tomfotirde, *SPE J.*, **15**, 139 (1959).
9. G. Martin, *Kunststofftechnik*, **11**(12), 324 (1972).
10. M. Gale, *Plast. Rubber Process. Appl.*, **2**, 347 (1982).
11. G. M. Gale and M. T. Penny, *SPE ANTEC*, **26**, 69 (1980).
12. O. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer-Polymer Miscibility*, Academic Press, New York, 1979.
13. D. A. Hemsley and M. Hayles, *The Development of a Microradiography Stage for Use in the SEM and Its Applications*. Inst. Phys. Conf. Ser. No. 36, 1977.
14. O. Ogbobe, PhD Thesis, Loughborough, LE11 3TU, U.K., 1985.
15. M. Ahmed, *Colouring of Plastics—Theory and Practice*, Van Nostrand Reinold, New York, 1979.
16. D. A. Hemsley, Institute of Polymer Technology, LUT, Loughborough, LE11 3TU, U.K., private communication.

Received August 28, 1991

Accepted November 19, 1991