Morphological Studies on Roll Extruded, Plasticized Composites

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SYNOPSIS

A study of the morphologies of polymer/carbon black composites, plasticized with small molecule organics, is presented. Four different plasticizers and three different polymers were used. In all cases, the plasticizers depress the T_g of the polymers. Whereas in some cases the organic small molecule was found to be molecularly dispersed in the polymer matrix, phase separation occurred in other cases beyond a certain composition. In the latter instances, the excess plasticizer formed crystalline aggregates and a depression of the melting point of the plasticizer was observed. The samples were prepared by a process similar to roll extrusion, which causes biaxial orientation of the crystalline aggregates.

INTRODUCTION

The rheology of polymers and copolymers containing carbon black has been reported by Lakdawala and Salovey[1] both in conditions in which the carbon black plasticizes the polymer and in conditions in which it does not. Invariably, in these composites, the carbon black reinforces the host polymer and increases its glass transition temperature. Plasticization is widely used in polymer technology for tailoring polymer properties for specific applications. The plasticization process often utilizes small molecule, crystallizable organics, which are either molecularly dispersed, or exist in crystalline aggregates in the composites. A depression of the T_g of the polymer usually accompanies such plasticization. Whereas the presence of the carbon black in the polymer resin is required for applications such as printing, it should be possible to modify the reinforcing effect of the carbon black by adding plasticizers as a third component. In this article, a study is presented of plasticized composites containing three different copolymers, carbon black, and small molecule plasticizers. The samples were prepared by a process similar to roll extrusion and were characterized by thermal analysis, microscopy, and x-ray diffraction. The roll extrusion technique for imparting orientation in semicrystalline polymer films, in order to improve mechanical properties, has been discussed extensively by Magill and coworkers.[2,3]

EXPERIMENTAL

The compositions of the three polymers used in this study, along with their glass transition temperatures, are given in Table I. The carbon black was a furnace black, Raven 5250. Three isomers of diphenylphthalate viz., o-diphenylphthalate (DPP, $T_m = 72°C$), m-diphenylisophthalate (DPIP, $T_m = 144°C$), p-diphenylterephthalate (DPTP, $T_m = 206°C$), and pentaeritritol tetrabenzoate (PETB, $T_m = 109°C$) were used as plasticizers. The polymer–plasticizer composites contained 20% of the latter. The polymer–carbon black–plasticizer composites contained 9% carbon black and 18% plasticizer. The composites were prepared by melt blending. The components were melted, mixed for several minutes, and passed through two rotating heated rollers operating at 155°C. The resulting sheets were cooled to room temperature. This preparation was carried out at Battelle Memorial Institute (courtesy of J. D. Robins).

**Table I The Compositions and Glass Transition Temperatures
of the Polymers Used in this Study**

| Polymer	Structure	Wt % Styrene	T_g (°C)
SBM65	Polystyrene/n-butyl methacrylate	65	62
SBM58	Polystyrene/n-butyl methacrylate	58	59
SIBM80	Polystyrene/isobutyl methacrylate	80	80

The thermal analysis was performed using a DuPont 990 thermal analyzer. The data were recorded during the second scan. The macro phase compatibility was estimated by visual observation of the time dependence on the transparency of the solid mixtures. These mixtures were prepared from known amounts of polymer and plasticizer, which were placed in a test tube, heated to liquefy both components, and were shaken for several minutes. The resulting composite melt was allowed to cool to room temperature and the clarity of the solid was monitored as a function of time. The time elapsed for the onset of visual cloudiness was noted. No quantitative turbidity measurements were made. Thin (1000 A) sections of the sheets for TEM observations were prepared using a DuPont Sorvall ultramicrotome and glass knives. A Philips EM400 transmission electron microscope, operating at 80

kV, was used to record the electron micrographs. Wide angle x-ray diffraction patterns were recorded using a Warhus flat plate camera (William Warhus Co., Wilmington, DE), with the x-ray beam (i) normal to the plane of the sheet, (ii) parallel to the plane and normal to the extrusion direction, and (iii) normal to (i) and (ii).

RESULTS AND DISCUSSION

Thermal Analysis

The thermal analysis of the polymers and the plasticizers showed that the T_m of the latter is higher than the T_g of the polymers, except for the SIBM80/DPP pair. The criterion that a single T_g should be observed for compatible composites was used to
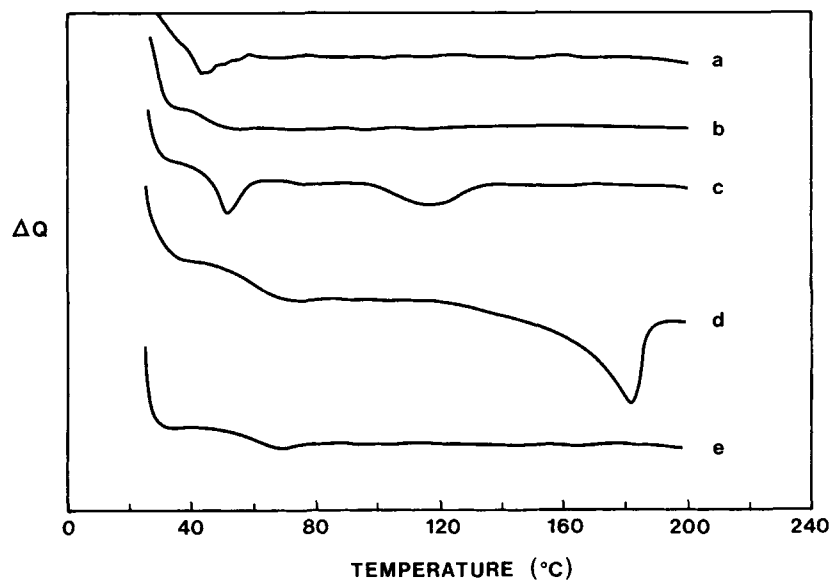

Figure 1 The DSC data are shown for the composites containing SBM58 polymer, carbon black, and the plasticizers: (a) DPP, (b) PETB, (c) DPIP, and (d) DPTP. The curve e corresponds to no plasticizer.
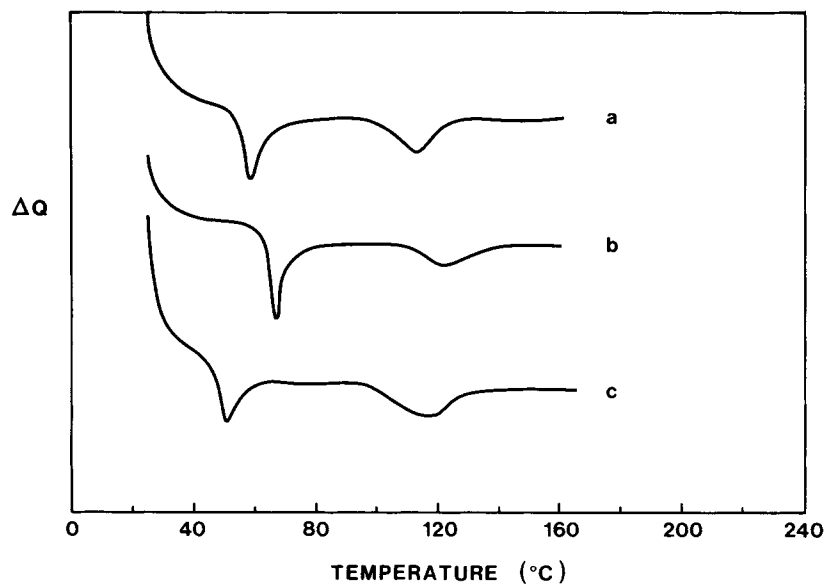
Figure 2 The DSC data are shown for composites containing DPIP and (a) SBM65, (b) SBM58, and (c) SIBM80.

characterize the composites. The DSC data for the composites containing SBM58 polymer, the carbon black, and different plasticizers are shown in Figure 1, along with data for a composite containing the polymer and carbon black but no small molecule plasticizer. Curves a–d show that the T_g of the poly-

mer has shifted to lower temperatures in all cases, compared with the case containing no plasticizer. This demonstrates that the plasticization takes place in these composites. It is also seen from curve e that carbon black alone increases the T_g of the polymer in this case, which is consistent with the reinforcing
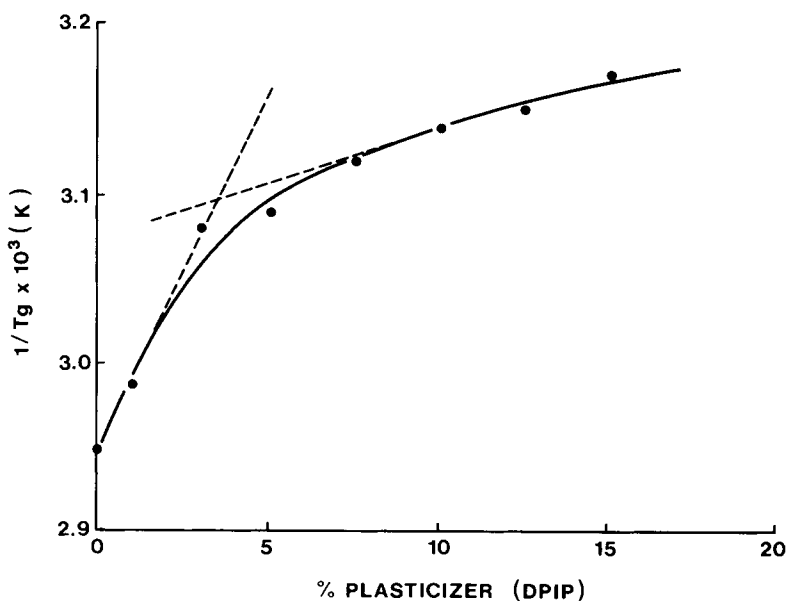
Figure 3 The depression of the T_g of the SBM58 polymer with various concentrations of the DPIP plasticizer.

a   **b**
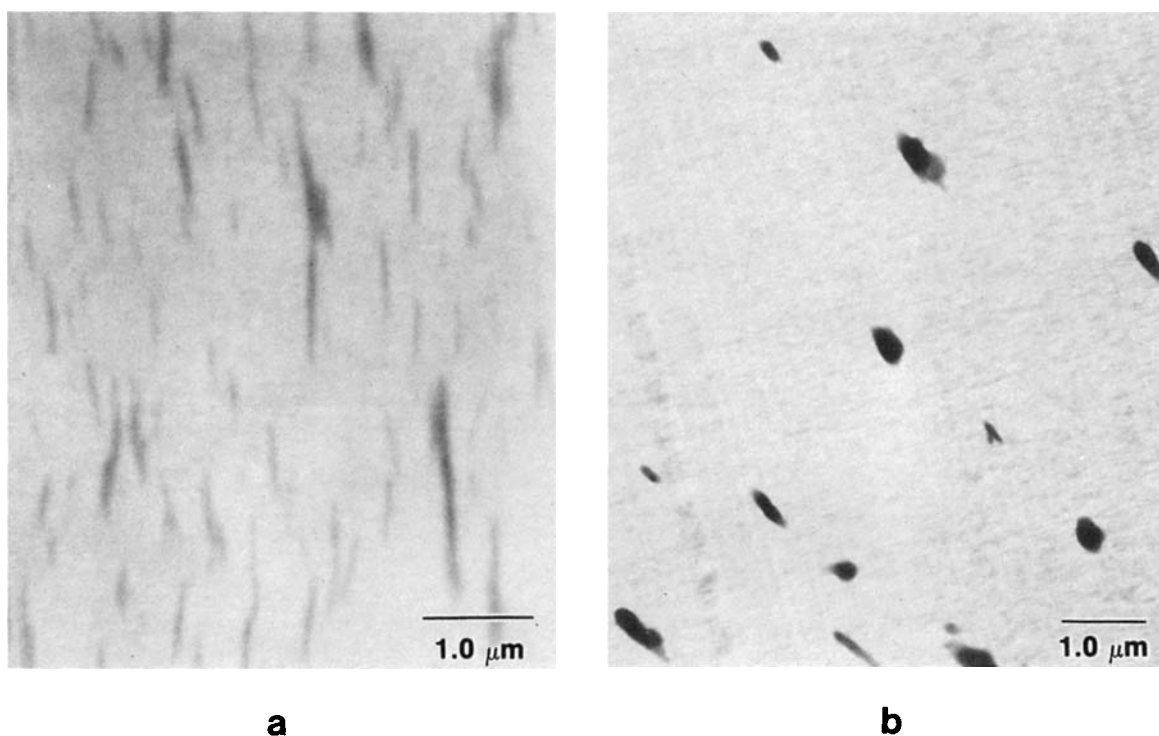
Figure 4 The transmission electron micrographs of thin sections of the composites containing DPIP and (a) SBM65 and (b) SIBM80 polymer.

effect of the carbon black.[1] In the thermograms corresponding to the composites containing DPIP and DPTP, a second transition is observed in addition to the T_g of the polymer, and this is attributed to the melting of the plasticizer. It is interesting to note that the T_m of the plasticizer is depressed by $\sim 20°$. Figure 2 shows the thermograms of the composites of the three polymers, with DPIP. It is seen that in all three cases, the T_m of DPIP is reduced by $\sim 20°C$. This could be attributed to the imperfection of ordering in these crystals. We believe that this is the first reported case of the depression of the T_m of the plasticizer in a composite.

The results in Figures 1 and 2 suggest that a phase separation occurs in the cases of DPIP and DPTP. The fact that even in these cases the T_g of the polymer is lowered can be explained by considering that only a fraction of the DPIP content acts as plasticizer and the rest separates into a distinct phase. To substantiate this interpretation, the T_g of the composites containing SBM58 polymer with varying concentrations of DPIP were measured and the data are shown in Figure 3. The curve of T_g depression with plasticizer content shows two slopes. The curve indicates a linear relationship up to a concentration

of 5% DPIP, and the effect is less pronounced above this concentration. The intersection of the two slopes of the curve in Figure 4 indicates the concen-

Table II   Visual Compatibility of Polymer Plasticizer Composites

Composite Components	Time of Appearance of Cloudiness (after solidification)
SBM 58 + DPIP	30 min
SBM 65 + DPIP	30 min
SIBM 80 + DPIP	30 min
SBM 58 + DPTP	During solidification
SBM 65 + DPTP	During solidification
SIBM 80 + DPTP	During solidification
SBM 58 + DPP	4 days
SBM 65 + DPP	4 days
SIBM 80 + DPP	6 days
SBM 58 + PETB	> 7 days
SBM 65 + PETB	> 7 days
SIBM 80 + PETB	> 7 days

Table III Dependence of Composites Visual Compatibility on Plasticizer Concentration

| Composite Components	Time of Cloudiness Appearance[a]
50% SBM 58 + 50% DPTP	During solidification
70% SBM 58 + 30% DPTP	During solidification
80% SBM 58 + 20% DPTP	During solidification
90% SBM 58 + 10% DPTP	2 min
50% SBM 58 + 50% DPIP	30 min
70% SBM 58 + 30% DPIP	< 4 days
80% SBM 58 + 20% DPIP	> 7 days
90% SBM 58 + 10% DPIP	> 7 days

[a] Time after solidification.

tration limit beyond which the plasticizer is no longer compatible with the polymer.

Visual Observations

Melt blends of the polymer and the plasticizers with 50 : 50 composition were prepared as described above. The time taken for macrophase separation in each case is given in Table II. In the case of the composites containing DPIP and DPTP, a macrophase separation was observed during solidification, or in 30 min, with the plasticizer exuding to the surface of the composite, forming two distinct layers. However, in the case of DPP, slight cloudiness (without discernable phase separation) occurred only after four days, while the PETB composite remained transparent even after a week. These observations agree with the results of the DSC measurements on composites with 20% or less of the plasticizer.

Table III shows the results of visual observations on composites containing various amounts of DPTP or DPIP and SBM58 polymer. The results for composites containing as little as 10% DPTP are in agreement with the DSC data. However, it is seen from Table III that for composites with DPIP concentration of $\leq$ 20%, no cloudiness or phase separation is observed, even after seven days. This finding is inconsistent with the DSC results, which suggested the presence of two components and, hence, two transitions. This apparent contradiction can be

a   b
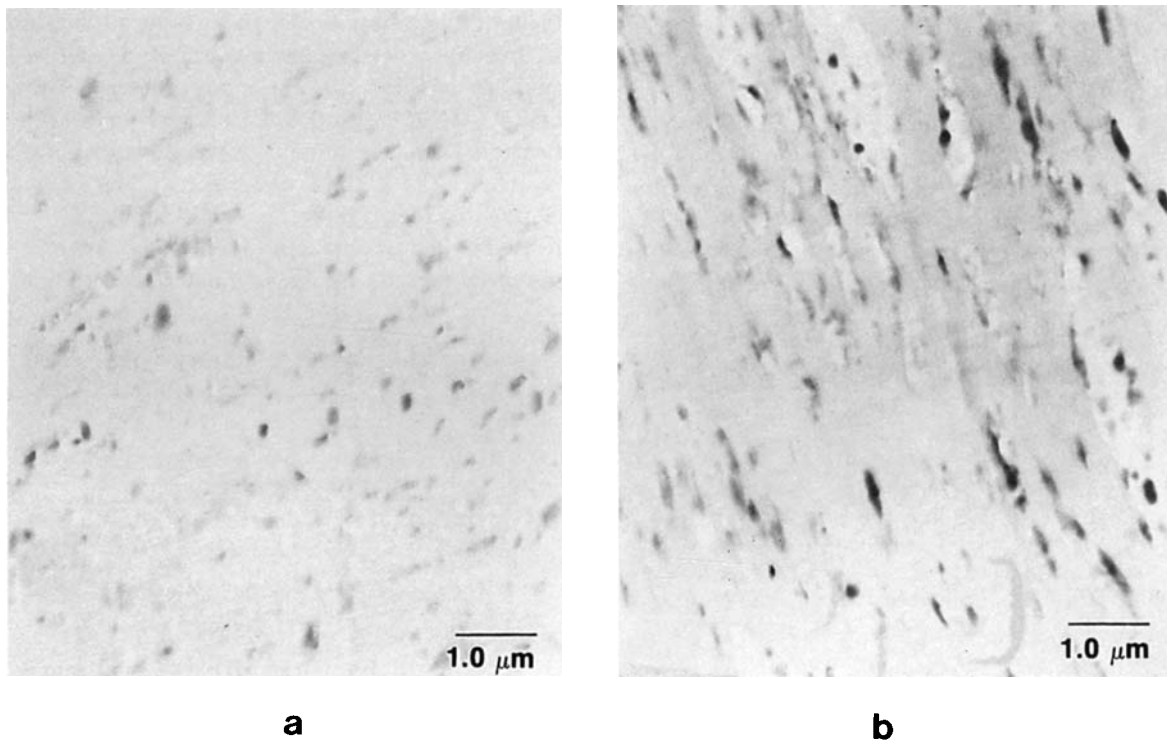
Figure 5 The transmission electron micrographs of thin sections of the composites containing DPTP and (a) SBM65 and (b) SIBM80 polymer.

explained on the basis that microphase separation does occur but it is below the visual limit. This explanation is supported by the results of electron microscopy and x-ray analysis.

Electron Microscopy

Transmission electron micrographs of thin sections (1000A) of the composites containing DPIP plasticizer in SBM65 and SIBM80, without carbon black, are shown in Figure 4. Elongated, small aggregates of DPIP, fairly uniformly distributed in the polymer matrix, are observed. Similar observations were made in the case of the SBM52 polymer. The micrographs corresponding to the DPTP in the same polymers are shown in Figure 5. The DPTP has separated from the polymer phase in well-distributed, small aggregates, but of a different shape and size. The composites containing DPP and PETB did not show the presence of any aggregates. Thus, it may be concluded that these two plasticizers are molecularly dispersed in the polymer matrix. These results corraborate the DSC data, which showed transitions corresponding to melting of DPIP and DPTP, but no melting in the cases of DPP and PETB. The crystalline nature of the aggregates was verified by electron diffraction, although it was difficult to record the patterns due to the beam sensitivity of the crystals. However, this was accomplished using x-ray diffraction.

Further observations made on the shapes and sizes of the aggregates from the micrographs are given in Table IV. In the case of DPIP, aggregates as long as 7.5μ were observed, whereas with DPTP, these aggregates were much smaller. An additional feature existed in that the long axis of the aggregates
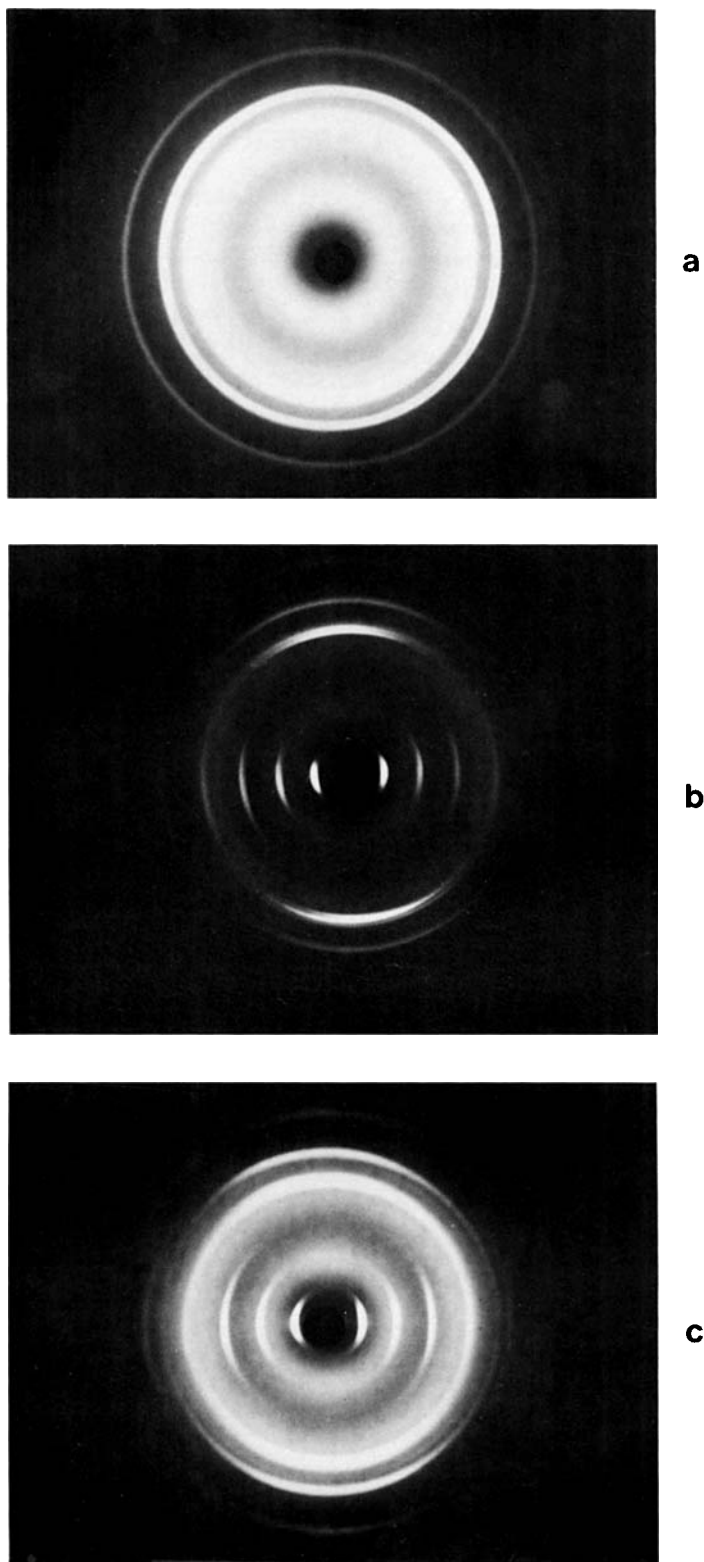
show orientation parallel to the extrusion direction. It was confirmed that the orientation was not caused by the microtome knife movement by selecting different directions for sectioning. Both elongation and orientation were thus induced due to the shear stress applied by the heated rollers during the preparation of the flat pieces of composites. Thus, one can expect that both the size of the crystallites and the orientation distribution can be tailored by varying the roll-extrusion conditions.

X-Ray Diffraction

The crystalline nature of the DPIP and DPTP aggregates was established by recording wide angle x-ray diffraction patterns. Figure 6 shows the diffraction patterns recorded in three directions for the composite containing DPTP and SBM58. Figure 6(a), which corresponds to the x-ray beam being normal to the sheet surface, shows crystalline reflections due to DPTP although no orientation is indicated. On the other hand, Figures 6(b) and (c), which were recorded with the x-ray beam parallel to the surface of the sheet, show orientation of the DPTP crystallites. Such an orientation, reflected in the x-ray patterns in the configurations corresponding to Figure 6(b) and (c), indicate biaxial orientation. The patterns shown in Figure 6 are similar to those recorded for biaxially oriented polymer films such as Mylar.[4] Similar x-ray patterns from the DPIP/SBM58 composites showed crystalline reflections, but the biaxial orientation was less pronounced. Thus, the orientation of the crystalline aggregates observed in the TEM analysis was confirmed by x-ray diffraction. The biaxial orientation observed for the DPTP composite shows that roll

Table IV   Characteristics of the Plasticizer Aggregates

Composites	Shape	Size (μ) ($l \times w$)	Distribution	Orientation
SBM 58 + DPIP	Elongated	(0.5–5) × (0.2–2)	Uniform	Oriented parallel to the long axis of the aggregates
SIBM 80 + DPIP	Elongated	(2.5–7.5) × (1–2)	Uniform	Oriented parallel to the long axis of the aggregates
SBM 65 + DPIP	Elongated	(0.5–2) × 1	Uniform	Oriented parallel to the long axis of the aggregates
SBM 58 + DPTP	Mixture of oval	2.5 × 1.5	Uniform	Oriented
SIBM 80 + DPTP	+ elongation		Uniform	Oriented
SBM 65 + DPTP			Uniform	Partialy oriented

Figure 6   X-ray diffraction patterns from DPTP/SBM58 composite: (a) the x-ray beam normal to the plane of the composite sheet; (b) the beam parallel to the plane of the sheet, and normal to the extrusion direction; (c) the beam parallel to the plane of the sheet and the extrusion direction.

extrusion would be a convenient method to achieve this morphology in plasticized polymer systems.

CONCLUSIONS

The study presented here shows that small molecule plasticizers can be incorporated in polymer–carbon black composites to tailor the T_g. The roll extrusion induces biaxial orientation of the crystalline aggregates of the small molecule plasticizer. In this article, we have not, however, examined factors such as the influence of the pressure, temperature, and speed of the rollers on the size and orientation distribution of the aggregates, nor the amorphous orientation, if any, of the polymer matrix.

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