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THERMAL ANALYSIS OF VAMAS POLYCARBONATE–POLYETHYLENE BLENDS *

SHU-SING CHANG

Polymers Division, Institute for Materials Science and Engineering,
National Bureau of Standards, Gaithersburg, MD 20899 (U.S.A.)

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ABSTRACT

Differential scanning calorimetry and thermogravimetric analysis were performed on a series of polycarbonate–polyethylene (PC–PE) blends, which were provided by the Technical Working Party of Polymer Blends, Versailles Project on Advanced Materials and Standards (VAMAS). Detailed comparison of results from cooperating laboratories were summarized and reported by W. Mielke [1].

The PC–PE blends were found to be immiscible. Intensive properties such as melting points and glass transition temperatures were found to be independent of the composition. Extensive properties such as specific heat, heat of fusion and ΔC_p of glass transition were found to be nearly proportional to the composition. Onset and residues of degradation at different stages in thermogravimetric analysis were also found to be a function of the composition. Multiple melting peaks of low density polyethylene and relaxation peaks of annealed PC glass transition were also studied.

INTRODUCTION

As part of the agreement of the Economic Summit of Versailles in January 1982, the Seven Heads of State and Government Representatives of the European Communities recommended collaboration on science and technology. The Versailles Project and Advanced Materials and Standards (VAMAS) is part of the Technology, Growth and Employment program leading from these agreements and recommendations. The objective of the present project is to encourage the setting up of codes of practice and specifications for advanced materials on an internationally coordinated basis. Such codes create the conditions for the rapid adoption of materials

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* Dedicated to a wonderful teacher and a tireless researcher in thermodynamics and thermochemistry, Professor Edgar F. Westrum, Jr., on his 70th birthday.

by industry. New materials enlarge technological perspectives and catalyze innovation.

The technical working party on polymer blends (TWP-PB) was formally created in April 1985. Following the 1985 TWP-PB meeting, an international research program on polycarbonate–polyethylene and polystyrene–poly(vinyl methyl ether) blends has been proposed.

The National Bureau of Standards participated in the U.S. National Working Group and took on some of the testing and research. This paper presents the results of investigation on the thermal analysis (differential scanning calorimetry and thermogravimetric analysis) of the VAMAS polycarbonate–polyethylene blends by the U.S. National Bureau of Standards. The results from all seventeen participating laboratories from six countries have been summarized by Mielke [1].

EXPERIMENTAL

Materials—VAMAS PC–PE blends

The polycarbonate–polyethylene (PC–PE) samples were compounded and extruded under the supervision of the Industrial Materials Research Institute, National Research Council, Canada. The polycarbonate (PC) is a Lexan RL 5230-111N from General Electric Company with a reported melt index of 9.5 g per 10 min and a density of 1.2 g ml^{-1}. The low density polyethylene (PE) is an Escorene LL 1030.28 from Esso Chemicals, Canada with a reported melt index of 0.5 g per 10 min, a density of 0.918 g ml^{-1} and 15.8 mol.% butane as co-monomer. Nine samples of extruded PC–PE blends were distributed, consisting of five 6 mm thick plaques of nominally 0%, 25%, 50%, 75% and 100% PC, and of four 2 mm thick plaques of nominally 0%, 25%, 50% and 75% PC.

The two pure polymers from the VAMAS samples, 0% polycarbonate (PC) or 100% polyethylene (PE), and 100% PC, appear to be uniform over the entire thickness and are relatively transparent compared with the blends. All blends, thin and thick, appear to be non-uniform with a five-ply configuration. The two surface layers and the center layer are more opaque, while the two layers between the surface and the center are more transparent. By bending the specimen a few times, these layers are easily delaminated. The appearances of the two surface layers are different; the surfaces of the specimens received were not labeled with "top" or "bottom" as produced. This layered structure and its associated chemical and/or physical differences may be related to some non-linearity in the temperature–time relationship during the manufacturing process.

Differential scanning calorimetry

A differential scanning calorimeter, Perkin–Elmer DSC-7 * was used in this study. A sample weight around 10 mg was enclosed in an aluminum capsule. A heating rate of 10 ° C $\min^{-1}$ was generally used.

Thermogravimetric analysis

A thermogravimetric analysis instrument, Perkin–Elmer TGA-7 *, was used in this study. A sample weight of 5–10 mg was used and the heating rate was 10 ° C $\min^{-1}$. Both air and N_2 were employed.

RESULTS AND DISCUSSION

Differential scanning calorimetry

Differential scanning calorimetry (DSC) experiments were performed using a heating rate of 10 ° C $\min^{-1}$ between 50 and 250 ° C. The sample was nominally 10 mg and was tightly encapsulated in an aluminum capsule. Some exploratory runs were also done using higher heating rates and wider temperature ranges. Except for the investigation of individual layers, all samples were cut perpendicular to the surfaces.

0% PC (100% PE)

The PE sample shows behavior typical of low density polyethylene with a melting peak at about 125 ° C. The melting range is very wide and the melting curve may consist of more than one peak depending on the thermal history during crystallization. Because of the wide melting range, the precise onset-temperature, melting point, and heat of fusion are difficult to determine. The temperature for the highest temperature peak, T_p, the heat of melting, ΔH_m, obtained by integrating the peak area from 60 to 130 ° C, and the temperature reaching the liquid state, T_L, are listed in Tables 1–3 as a relative indication only. These DSC temperatures are sensitive not only to the nature of the sample and the heating rate but also, somewhat, to the sample size. The heat of fusion and the melting temperatures are generally lower after a fast-cooling procedure and higher after slow cooling from the melt. The results on the thin and the thick samples are listed in Tables 1 and 2, and shown as the top curves in Figs. 1–4.

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* Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply necessarily the best available for the purpose.

TABLE 1

DSC results of thin (2 mm) VAMAS PC–PE samples

χ (%PC)	Condition [a]	T_1 (°C)	T_p (°C)	ΔH_m (J g^{-1})	T_L (°C)	T_g (°C)	T_x (°C)	Q_x (J g^{-1})
0	AR		126	98	131			
	FC		124	96	129			
	SC		127	102	132			
25	AR		124	72	129	150	219	−3
	FC		122	73	126	147		
50	AR	91	125	49	128	151	220	−3
	FC		123	48	126	147		
75	AR	110, 121	129	27	134	151	(180)	
	FC		123	25	126	149		
	SC	110, 120	126	26	130	150		

[a] Condition codes: AN, annealed; AR, as received; FC, fast-cooled; SC, slow-cooled; STC, step-cooled; VSC, very slowly cooled.

Temperatures in parentheses denote the approximate location of broad or weak thermal events.

By cooling PE (0% PC) from 150 °C to 60 °C in steps of 30 °C and holding at each temperature for 15 min, a complicated melting behavior may be observed for the resulting solid, with melting peaks at 68 °C, 88 °C, 97 °C, 120 °C, and 127 °C, see Fig. 5. The total heat of melting is, however, of a magnitude similar to that of the same sample with different thermal

TABLE 2

DSC results of thick (6 mm) VAMAS PE–PE samples

χ (%PC)	Condition [a]	T_1 (°C)	T_p (°C)	ΔH_m (J g^{-1})	T_L (°C)	T_g (°C)	T_x (°C)	Q_x (J g^{-1})
0	AR		123	104	128		207	−5
	FC		123	98	127			
25	AR	(106)	123	81	127	148	217	−5
	FC		122	75	125	146		
50	AR	112	126	49	131	149	217	−2
	FC		123	48	128	148		
75	AR	114	123	24	127	148	216	−4
	FC		122	24	125			
100	AR					148		
	VSC					147		
	AN					147		
	FC					147		

[a] See Table 1 for condition codes.

TABLE 3

DSC results of thick (6 mm) VAMAS PC–PE samples at 20 °C min^{-1}

χ (%PC)	Condition [a]	T_1 (°C)	T_p (°C)	ΔH_m (J g^{-1})	T_L (°C)	T_g (°C)
0	AR		124	98	132	
	FC		122	84	130	
	STC	68, 88, 97, 120	128	95	134	
50	AR	115	127	48	133	154
	FC		123	44	129	148
100	AR					150

[a] See Table 1 for condition codes.

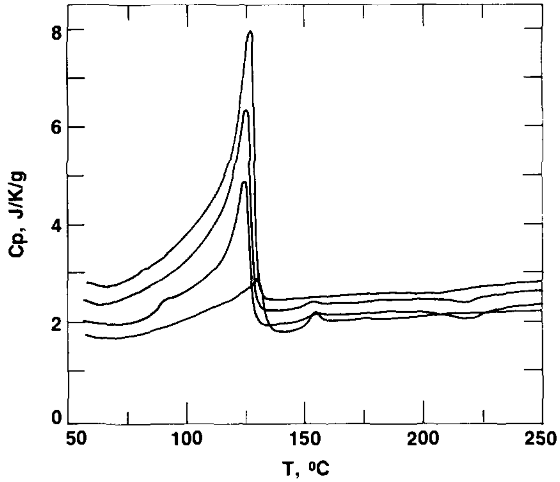

Fig. 1. DSC scans of 2 mm VAMAS PC–PE samples as received. Curves from top: 0% PC, 25% PC, 50% PC, 75% PC.

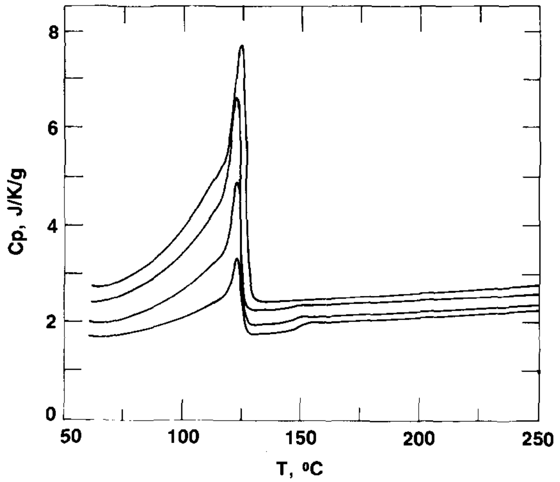

Fig. 2. DSC scans of 2 mm VAMAS PC–PE samples after fast-cooling from 250 °C. Curves from top: 0% PC, 25% PC, 50% PC, 75% PC.

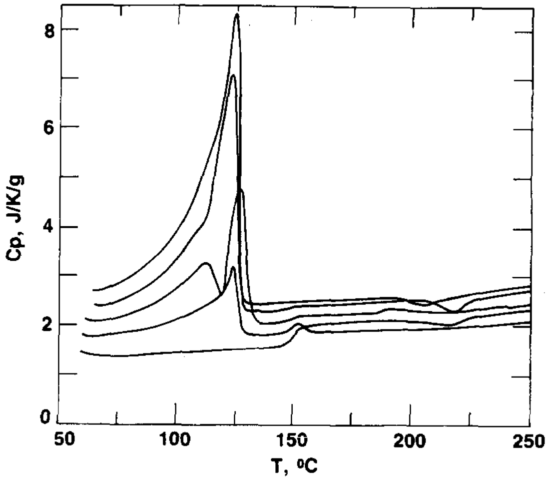

Fig. 3. DSC scans of 6 mm VAMAS PC–PE samples as received. Curves from top: 0% PC, 25% PC, 50% PC, 75% PC, 100% PC.

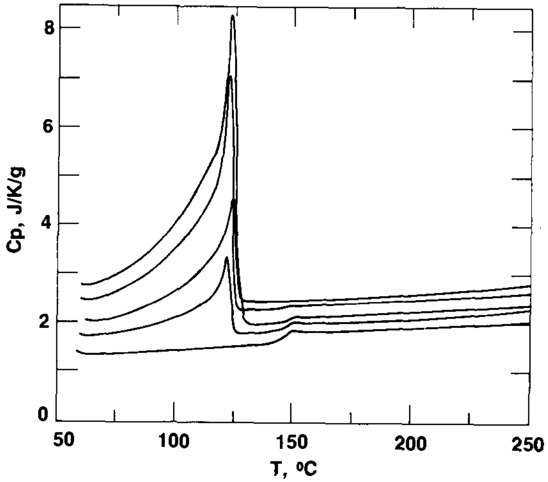

Fig. 4. DSC scans of 6 mm VAMAS PC–PE samples after fast-cooling from 250 ° C. Curves from top: 0% PC, 25% PC, 50% PC, 75% PC, 100% PC.

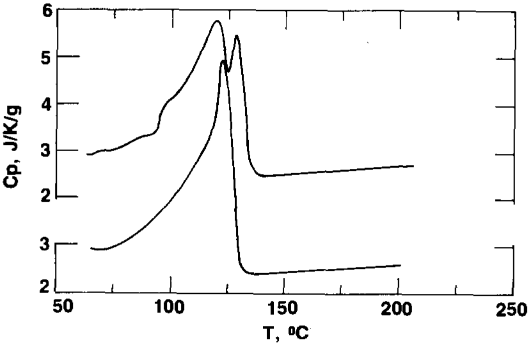

Fig. 5. Melting behavior of 100% PE (0% PC). Top curve: cooled from 150 ° C in 30 ° C steps. Bottom curve: fast-cooled.

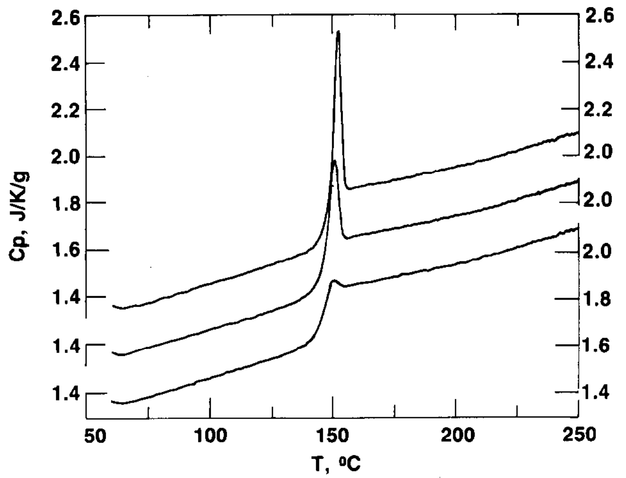

Fig. 6. Glass transition region of 100% PC. Top curve: cooled at 6 °C h^{-1} from 180 °C. Middle curve: annealed for 2h at 140 °C. Bottom curve: fast-cooled.

histories. Similar behaviors were found in branched polyethylene [2–5] and in other thermoplastics [6,7]. A hump in some of the DSC curves between 40 and 60 °C may be the result of long storage at room temperature.

100% PC

The T_g of the PC (6 mm only) used in the VAMAS blends is about 148 °C. The results are listed in Table 2, and shown as the bottom curves in Figs. 3 and 4. Relaxation peaks were observed for slow-cooled or annealed samples, see Fig. 6. T_g, or the fictive temperature, is defined by the intercept of the enthalpy curves below and above the glass transition [8]. T_g so defined is independent of the rate of observation and is dependent only on the rate at which the glass is formed from the liquid state. Normally, for fast-cooled samples not showing a relaxation peak, this is equivalent to the temperature midway in the C_p discontinuity. T_g or fictive temperature is lowered in the case of an occurrence of a relaxation peak. T_g for polycarbonate was determined at 142 °C with a ΔC_p of 0.25 J K^{-1} g^{-1} by adiabatic calorimetry [9]. The melting region for semi-crystalline polycarbonate was observed between 200 and 265 °C [9]. No melting of PC was detected in these VAMAS samples up to 380 °C, other than a slight thermal effect due, possibly, to some stress relaxation or decomposition.

Blends

All blends containing PE show a characteristic melting of the low density polyethylene, seen in Figs. 1–4 as well as in Figs. 7 and 8. The melting ranges are the same as that of 0% PC (100% PE). The variation in the highest peak temperature is an indication of the sample history rather than the experimental uncertainty. Most melting curves for the PE component in the

TABLE 4

DSC results of layers of thick (6 mm) 50% PC sample

Condition[a]	T_1 (°C)	T_p (°C)	ΔH_m (J g^{-1})	T_L (°C)	T_g (°C)	T_x (°C)	Q_x (J g^{-1})
AR	112, 121	125	53	128	148	207	−18
FC		122	50	125	145		
AR	112 (112)	125	53	128	149	217	−9
FC		121	50	125	146		
AR	111 (121)	125	52	128	148	220	−6
FC		121	50	124	146		
AR	110 (120)	124	52	126	147	223	−7
FC		121	49	124	146		
AR	110	123	51	127	149	209	−5
FC		121	50	124	144		

[a] See Table 1 for condition codes.

blend show a double peak when the samples were run as received. Subsequent runs after a continuous fast cooling process will generally yield a single peak. The temperatures of these lower temperature melting peaks are denoted by T_1 and listed in Tables 1–4. The heat of fusion obtained by integrating the entire peak region from 60–130 ° C, is proportional to the PE content, see Tables 1–3.

The glass transition temperature for the PC component in all the samples containing PC remains at 145–150 ° C, regardless of the composition, see Figs. 1–4 and 6–8. ΔC_p at T_g is roughly proportional to the PC content.

The C_p of the blends increases as the PE content is increased, see Figs. 1–4. The change in C_p is nearly proportional to the composition within the differences in C_p between PC and PE.

A small exothermic peak often appears around 200 ° C in the first run, see Figs. 1, 3 and 7. This exothermic peak disappears in subsequent runs as shown in Figs. 2, 4 and 8. The peak occurs in a temperature range of 205–225 ° C with a broad exothermic range of 180–240 ° C. A small amount of heat is released (mostly in the range of 2–7 J g^{-1}, calculated from a total heat effect of 20–50 mJ per sample). The peak temperature, T_x, and energy releases, Q_x, are listed in Tables 1, 2 and 4. It seems unlikely that this amount of energy is the release of a strain energy from pinching the aluminum sample capsule. A newly enclosed empty sample capsule and another capsule with a sapphire pellet failed to show any exothermic effects. The capsule containing the sapphire was deformed by the thickness of the sapphire pellet as were many of the capsules containing VAMAS samples. The possibility that this exothermic heat is from a crystallization effect for PC can be ruled out, since a similar phenomenon was observed for one of the PE samples. Whether this exothermic thermal effect comes from the relief of the residual strain in the sample produced during the manufacturing process, or from the DSC sample preparation by cutting and encapsulation, has not been determined. The storage of mechanical energy has been observed. On cold-drawn polycarbonate in the glassy state, a change of 25 J g^{-1} was observed in the energy increment between the glassy and the supercooled liquid states [10]. A residual stored energy from pelletizing poly(vinyl chloride) powders was found to be of the order of 3–4 J g^{-1} [11,12].

Another peculiarity was found during the crystallization of PE in the blends. Slow cooling of a 75% PC sample at 1 °C min^{-1} yielded two distinct exothermic peaks at 116 °C after a T_g of 143 °C. The heat of crystallization was estimated to be 22 J g^{-1} or about 90 J g^{-1} of PE, within 10–15% of the observed heat of melting.

The results of DSC runs at 20 °C min^{-1} and wider temperature ranges are listed in Table 3 for comparison purposes with the above observations.

Layers of 50% PC blend

Individual layers were separated from the thicker 50% PC sample. Although there appeared to be some differences in the melting behavior of PE, and in the T_g of PC and the 200 °C exotherm for the first DSC runs of each of the five layers (Fig. 7), subsequent runs following a similar fast-cooling procedure are virtually identical regardless of the position of the layer (Fig. 8). Therefore, all the layers appear to have a similar composition but have different initial physical properties, due perhaps to the manufacturing process.

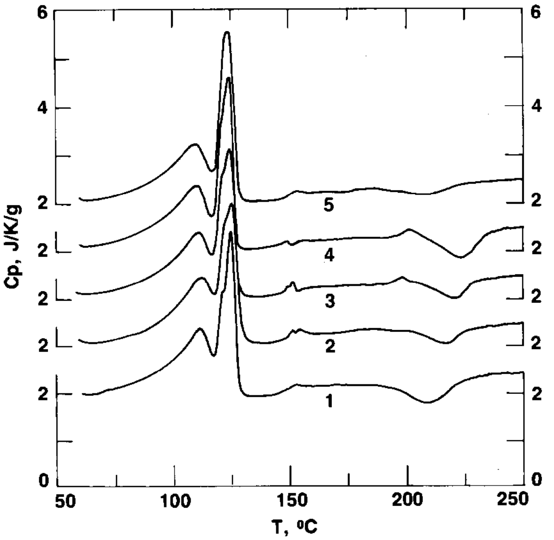

Fig. 7. First DSC scans of layers of 6 mm 50% PC sample.

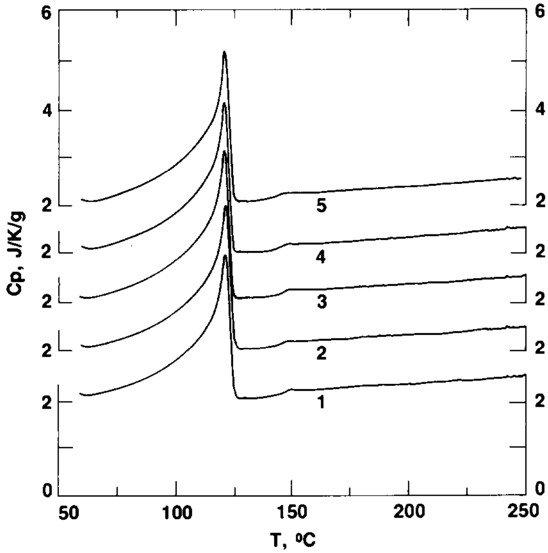

Fig. 8. DSC scans of layers of 6 mm 50% PC sample.

TGA—thermogravimetric analysis

All test samples were cut perpendicular to the surface through all layers of the particular specimen in order to be more representative of the overall composition. The sample size was generally from 5 to 10 mg. The heating rate used was 10 °C min^{-1}. TGA measurements were performed in air in order to assess the stability and to determine the usable temperature range, as most of the material would be used in a normal atmosphere, see Figs. 9 and 10. For thermal degradation studies, however, the kinetics are generally studied in N_2, see Figs. 11 and 12. The curves in N_2 are far more smooth than those in air.

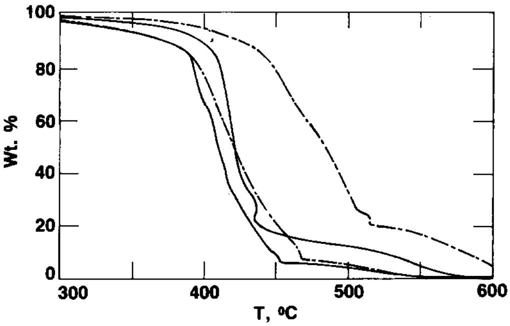

Fig. 9. Thermogravimetric analysis of 2 mm VAMAS PC–PE samples in air. Curves from top: 100% PC, 75% PC, 50% PC, 25% PC.

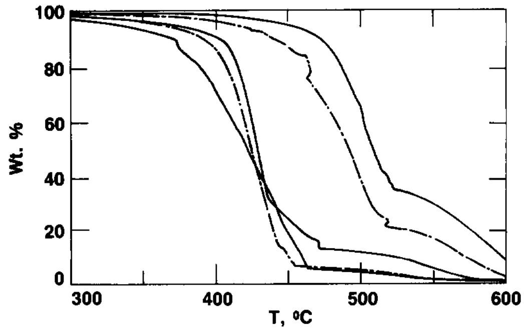

Fig. 10. Thermogravimetric analysis of 6 mm VAMAS PC–PE samples in air. Curves from top: 100% PC, 75% PC, 50% PC, 25% PC, 0% PC.

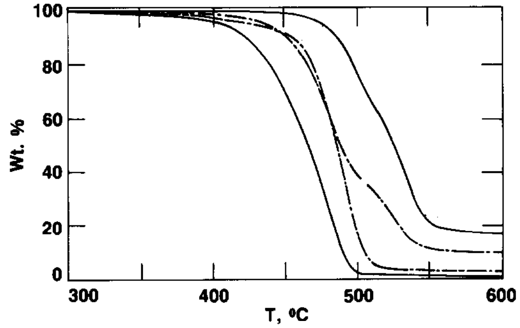

Fig. 11. Thermogravimetric analysis of 2 mm VAMAS PC–PE samples in N_2. Curves from top: 100% PC, 75% PC, 50% PC, 25% PC.

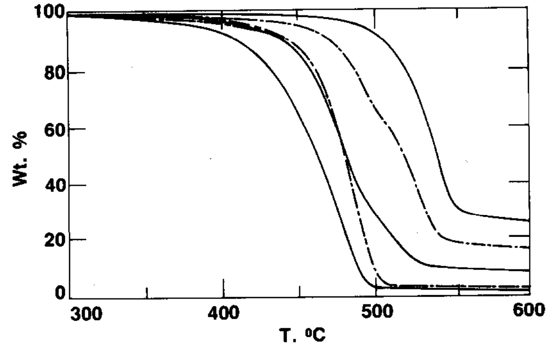

Fig. 12. Thermogravimetric analysis of 6 mm VAMAS PC–PE samples in N_2. Curves from top: 100% PC, 75% PC, 50% PC, 25% PC, 0% PC.

TABLE 5

Thermogravimetric analysis of VAMAS PC–PE samples

χ (%PC)	T_c (°C)	W_c (%)	W_r (%)
In air			
Thin (2 mm) samples			
0	455	6	0.4
25	470	7	0.3
50	450	17	0.0
75	518	20	0.0
Thick (6 mm) samples			
0	463	5	0.1
25	454	6	0.3
50	472	12	0.2
75	519	21	0.1
100	522	35	0.0
In N_2			
Thin (2 mm) samples			
0	496	3	0.5
25	505	4	0.4
50	531	10	0.2
75	546	19	0.0
Thick (6 mm) samples			
0	491	3	0.4
25	501	3	0.4
50	520	10	0.3
75	539	18	0.1
100	551	29	0.0

At a scan rate of 10 °C min^{-1}, weight loss began at about 200 °C for 0% PC (100% PE) and at about 375 °C for 100% PC in air, and at 300 °C and 430 °C, respectively, in N_2. No residue, W_r, was found in the PC sample. Residues (a whitish powder after 700 °C in air) of up to about 0.5% were found in samples containing PE. The end of the major degradation, leaving a completely charred material, occurred quite sharply at temperatures, T_c, ranging from about 450 °C to 520 °C. T_c was observed at higher temperatures for samples of higher PC content together with higher residues, W_c at T_c, see Figs. 9–12. Table 5 summarizes all the TGA results.

CONCLUSION

The VAMAS blends were made from low density polyethylene and a polycarbonate of low or negligible crystallinity. The components, PC and

PE, are probably completely immiscible judging from the following observations.

The glass transition region of the blends remained at 145–150 °C (similar to that of pure polycarbonate) in all compositions containing PC, with a ΔC_p of glass transition proportional to the PC content. For compatible blends, T_g of the blend is a function of the composition, and varies between the values of T_g of the two pure components. The melting temperature of the blends remained at about 125 °C (similar to that of pure low density polyethylene) for all compositions containing PE, with the heat of fusion ΔH_m being proportional to the PE content. This indicates that the blends are physical mixtures.

Although the different layers of a sample have different appearances and physical properties, their chemical compositions seem to be identical. Likewise, identical physical properties may be obtained through identical thermal histories.

A small broad exotherm at about 210 ± 10 °C appears in many samples during the first DSC run. Whether or not this exothermic peak is related to the relief of residual strain remains undetermined.

The relative thermal stabilities of PC and PE are evident from degradation studies in air and in N_2. Thermal analytical techniques have been shown to be useful in the study of the composition and thermal history of the blends.

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