

STUDIES ON POLY(ETHYLENE TEREPHTHALATE)/COTTON BLENDS BY DIFFERENTIAL SCANNING CALORIMETRY

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DSC curves of polyester/cotton blends indicate that the glass transition temperature, T_g , of cotton varies with the blend composition. Standard curves for quality control purposes are presented and are based on either the cotton or PET transition peak areas. Factors that contribute to the size of the peak areas were determined: a composition coefficient factor and a thermal coefficient factor.

Polymers are often blended to enhance some desirable properties, and in the textile industry cotton is often blended with other fibres, e.g. polyester, poly(ethylene terephthalate) (PET), because the former lacks crease resistance, dimensional stability, etc., while the latter is used extensively in the garment industry because of its durability, easy-care properties and ability to give brilliant shades. 100% PET, however, tends to be uncomfortable; it also has poor thermal properties and low moisture inhibition a quality undesirable in fabrics used in the tropics. It has therefore become increasingly important to use PET and cotton in blends and thus necessary to evolve a technique for the quick analysis of polyester-cotton blends for quality control purposes. David and King [1] tried to establish a simple density method for the analysis of fabric blends of polyester/cotton. The method requires a prior knowledge of the density of the polyester and that of cotton.

Iyer and Yer [2], attempting an IR technique, observed that the particle size is significant in the peak intensity of the 1725 cm^{-1} band (C=O) stretching in the polyester. This absorption band is recommended for the analysis of cotton-polyester blends. The method of sample preparation can affect the band width and hence the results.

However, IR spectroscopic analysis can be quite tedious and often lead to inconsistencies, and is therefore not critically definite. It is therefore intended in this present work to carry out the thermal analysis of polyester/cotton blends using a differential scanning calorimeter (DSC-2) in attempt to find an alternative technique for the quick analysis of the composition of cotton blends.

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Experimental

Annealing of poly(ethylene terephthalate)

This was done by winding some lengths of the fibre on aluminium foil and heat-setting them in a furnace at the required temperatures of 200° and 240° respectively, for three minutes. Sample preparation of the mixture: The cross-linked cotton samples mixed in various percentage compositions with annealed PET were pulverized in an agate mortar. A Perkin Elmer Differential Scanning Calorimeter (DSC-2) was used to determine the glass transition temperature (T_g) of the mixed samples.

Approximately 5 mg of the pulverized mixture was encapsulated in an aluminium sample pan. An empty gold pan was used as reference pan. Measurements were performed in nitrogen atmosphere at a heating rate of 20°/min and sensitivity range of 20 m cal/sec. The T_g values from the DSC curves were identified as the temperatures midway between the onset of the two linear portions before and after the transition period [3].

Results and discussion

Transition temperatures and peak area

Figure 1 shows a typical DSC curve for a polyester/cotton blend. The portion *A* of the curve refers to the cotton second-order transition, and T_g is determined as shown. The portion *B* refers to the melting transition of PET. The melting transition temperature (T_m) is determined as shown and occurs at about 250°.

The areas under the portions *A* and *B* give a measure of the energy involved in such transitions. The ordinate displacement of PET gives a measure of the rate of its transition as well as the heat capacity.

In most cases, the cotton transition peak is rather broad, making accurate determination of peak height and hence ordinate displacement rather difficult. Therefore, only the ordinate displacement for PET, which gave a sharp transition, was determined.

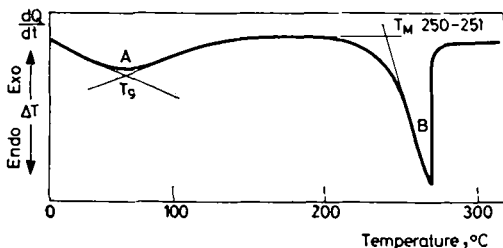


Fig. 1. Typical DSC curve for a polyester-cotton blend Scan rate: 20°/min, Range: 20 mcal/sec

Figure 2 was obtained by plotting the temperature of the cotton transition peak against the blend composition. At 100% cotton, the T_g values of Samaru 72 cotton (S'72) and cross-linked PET/Samaru 72 blend (XS'72M) are 91° and 90°, respectively, while those of Samaru 77 (S'77) cotton and cross-linked PET/Samaru 77 cotton blend (XS'77M) are 89° and 98°, respectively. These differences in

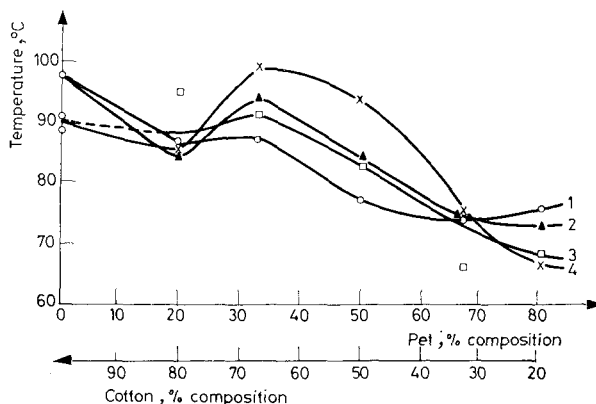


Fig. 2. Effect of blend composition on T_g of crosslinked cotton ○ Curve for change in T_g with blend composition of XS77M and PET annealed at 200°; ▲ Curve for change in T_g with blend composition of XS77M and PET annealed at 240°; □ Curve for change in T_g with blend composition of XS72M and PET annealed at 200°; × Curve for change in T_g with blend composition of XS72M and PET annealed at 240°; - - - Most probable temperature for 200° PET and XS72M at 20/80 blend composition

T_g for the two types of cotton seem to indicate a difference in structure between the two cotton varieties. It has been inferred [4], that S'77 may be less crystalline than S'72, and S'77 may possess a structure susceptible to a greater alkali swelling and subsequent cross-linking actions than S'72, and hence the high value of T_g for XS'77M. The higher value of T_g for cross-linked cotton than for pure S'77 is expected, because cross-linking enhances the stiffness of the cotton. This stiffness imposes a restriction on the chain flexibility and consequently leads to a high T_g . The initial decrease in T_g for 0–20% cotton/PET mixtures suggests that the effect of cross-linking becomes occluded in the mixture, perhaps because of the presence of PET, which imposes a more significant influence.

In the 20/80 PET/cotton mixture there is apparently no influence of cotton varietal differences on the cotton transition temperature. The transition for different cottons mixed with PET previously annealed at two different temperatures seems to occur consistently at the same temperature. However, the temperature at which the PET was annealed appears not to be significant at this blend composition.

From the 20/80 PET/cotton mixture to the 33/67 PET/cotton mixture there is a rise in T_g until an optimum value is reached at the 33/67 PET/cotton mixture. Also

the transition becomes dependent on the cotton variety as well as the temperature at which the PET in the mixture was annealed. The highest transition is observed for S'72 mixed with PET at the 33/67 PET/cotton composition previously annealed at 240°. For the 67/33 PET/cotton mixture, the transition like those for 20/80, appears consistently independent of both cotton variety and the previous heat treatment of the PET in the mixture. However, the transition occurs at a lower temperature as compared to those for the 20/80 mixture composition. It should be noted that 67/33 PET/cotton is the usual commercial blend composition.

The trend in the change of the T_g of the cotton in the PET/cotton mixture suggests a kind of surface interaction between the cotton and the PET component, the resultant effect of which causes the T_g to behave in the manner shown in Fig. 2. As the % PET in the mixture is increased, the cohesive forces are maximized in the 33/67 PET/cotton blend and decrease as the PET fraction is further increased. Thus, the cotton fraction and the previous thermal history of the PET seem to play significant roles in the degree of cotton transition. Generally, therefore, the lower the cotton fraction in the blend, the lower the surface 'interaction' and the higher the previous heat-setting temperature of the PET, the higher the 'interaction' (cohesive force).

Landel [5] studied the temperature-dependence of the dynamic mechanical properties of a polyisobutylene-glass bead system, and found an increase in T_g of

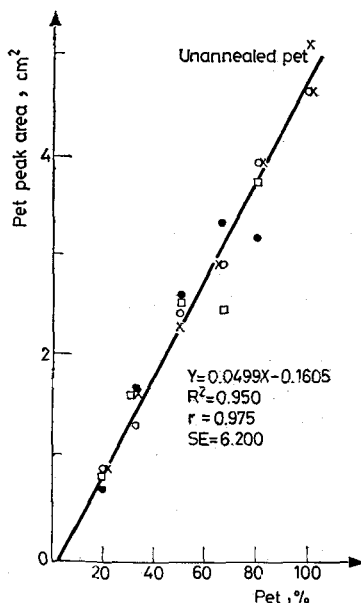


Fig. 3. Effect of % polyester/cotton blend on the peak area polyester (PET) annealed at 200 and 240°

● PET S77 } 240° □ PET S72 }
× PET S72 } ○ PET S77 } 200°

about 2, 6 and 7° for systems containing 8.86, 20.3 and 36.7 vol % beads, respectively. Since the glass beads were non-reinforcing, he considered these increases to be reasonable and related them to a possible small amount of cross-linking caused by polymer adsorption. Similar behaviour might perhaps be possible for a PET/cotton blend, especially at elevated temperatures.

Figure 3 shows the effect of the PET fractions in the PET/cotton blend on the peak area of the PET transition. In the plots it is assumed that the peak area is independent of the previous thermal history of the PET component as well as the cotton variety. Application of the least square method to obtain the best straight line plot from the experimental data at the two temperatures used in the study shows that the values regress well to give linear equations. For Fig. 3:

$$Y = 0.0499 X - 0.1605 \quad (1)$$

Figure 4 gives the effect of the annealing temperature of the PET on the cotton peak area in PET/cotton blends. These plots were obtained from the equation:

$$Y = 0.092 X - 0.0204 T + 3.183 \quad (2)$$

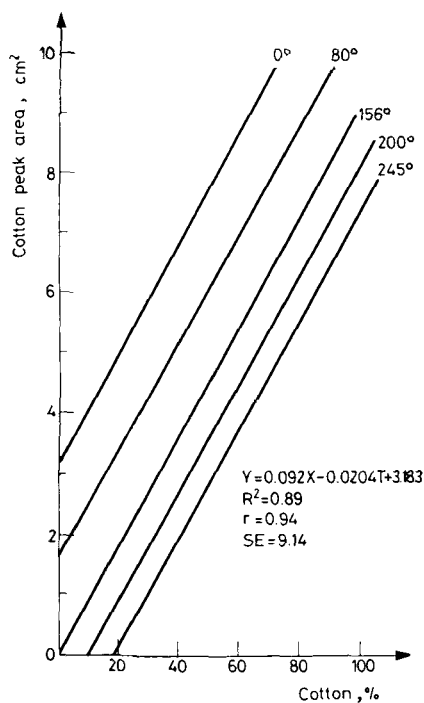


Fig. 4. Effect of annealing PET temperature on the cotton peak area in cotton-polyester blend.
 X = % composition; Y = cotton peak area; T = annealing temperature of PET

(i.e. X and Y were regressed as a function of temperature.) The linear plots obtained therefrom indicate that the peak areas differ for mixtures containing PET annealed at different temperatures. For a given PET/cotton composition, the lower the annealing temperature of PET, the greater the peak area.

A standard plot is possible at 156°. Therefore, if cotton of given variety is blended with PET previously annealed at 156°, a linear plot of peak area versus % cotton composition would be obtained, which passes through the origin for various cotton fractions in a PET 156°/cotton blend. Thus, if the curves are obtained for unknown PET/cotton blends, the cotton peak area can be determined, and the % cotton and hence PET can be obtained from the standard curve. It should be noted that the workability does not necessarily require that the PET in the PET/cotton blend be annealed. The slopes of the plots in Fig. 4 are the same and unchanged with the annealing temperature, indicating that the rate of transition for the cotton is consistent irrespective of the PET annealing temperature. Therefore, extrapolation from any experimental point to the standard curve would give the % cotton and hence % PET in such a blend.

Figure 5 shows the effect of the annealing temperature on the PET peak area in PET/cotton blends. The plots were obtained from a regressed equation of X and Y as a function of temperature, given as:

$$Y = 0.413 + 0.0463 X - 0.00177 T \quad (3)$$

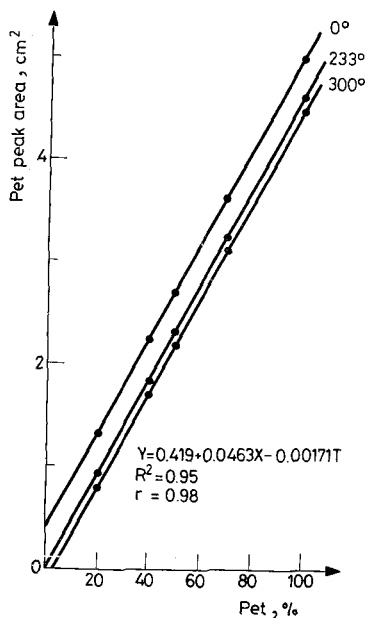


Fig. 5. Effect of annealing PET temperature on the peak area in polyester/cotton blend.
 Y = PET peak area; X = % composition; T = annealing temperature of PET.

Where $Y =$ PET peak area, $X =$ PET fraction in the mixture, and $T =$ PET annealing temperature.

Just as was clearly shown in Fig. 4, it is also observed in Fig. 5 that at any given blend composition the peak area decreases with increase in the annealing temperature of the PET. At 233° a plot passing through the origin is obtained and could be used as a standard curve. Thus, if curves are obtained for unknown PET/cotton blends, the PET peak area can be obtained for unknown PET/cotton blends, the PET peak area can be determined, and then the % PET and hence % cotton can be obtained from the standard curve.

From Figs 4 and 5 it is concluded that a standard curve is possible, based on either the cotton peak area or the PET peak area component of the PET/cotton blend from the DSC curve. The fact that the two curves occur at different annealing temperatures, i.e. 156° when considering the cotton transition only, and 233° when considering the PET transition alone, is indicative of the difference in degree of the influence of cotton on PET and vice versa. This influence is to a large extent determined by the previous thermal history of the PET in the PET/cotton blends.

Figure 6 shows the rate of transition based on the ordinate displacement of the PET transition. The ordinate signal represents energy/unit time or power. Generally, from 0 to 67% PET composition the rate of transition increases rapidly

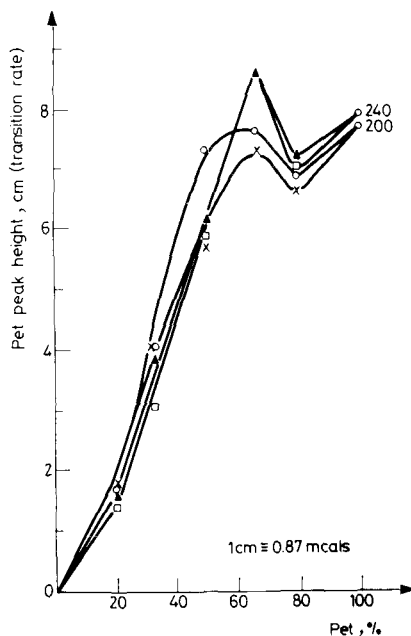


Fig. 6. Effect of blend composition on the PET peak height (transition rate). ▲ PET S72 cotton at 240° ; □ PET S77 cotton at 240° ; □ PET S77 cotton at 200° ; × PET S72 cotton at 200°

and reaches an optimum at 67% PET composition, after which a decrease is observed. The rate of transition is therefore more dependent on the PET annealing temperature and more influenced by the mixture composition than the cotton variety. It could be that at high cotton composition the interactions with PET cause a rapid first-order transition of the PET. It could also be that the cotton component takes a smaller amount of the heat supplied to the blend, the rest being taken up by the PET. The heat supply rate is constant, and therefore when the PET fraction is small, a greater amount of heat is available to it than when a large PET fraction is present. This consequently leads to a more rapid PET transition at high PET content, although this argument breaks down after the 67/33 PET/cotton blend composition, where a slight decrease is observed.

Thermal coefficient, T_{Coeff} , and composition coefficient, C_{Coeff} .

In Fig. 4, the plots at different temperatures have the same gradient. This is observed again from the fact that the linear plots are parallel. This gradient is called the composition coefficient and may be represented as follows:

$$C_{\text{Coeff}}^{\text{Cot}} = \frac{dY}{dA_{\text{Cot}}}$$

or

$$C_{\text{Coeff}}^{\text{Cot}} dA = dY_{\text{Cot}} \quad (4)$$

Where dA is the change in the cotton component in the PET/cotton blend;

$C_{\text{Coeff}}^{\text{Cot}}$ is the composition coefficient, which is independent of temperature.

Similarly, the gradients of the plots in Fig. 6 are constant and give an indication of the thermal coefficient of the system. As observed from the plots, the thermal coefficient is independent of the blend composition. The activation energy is therefore independent of the blend composition. The thermal coefficient is given as:

$$T_{\text{Coeff}}^{\text{Cot}} = \frac{-dY_{\text{Cot}}}{dTemp}$$

$$(T_{\text{Coeff}}^{\text{Cot}}) dTemp = -dY_{\text{Cot}} \quad (5)$$

where $T_{\text{Coeff}}^{\text{Cot}}$ is the thermal coefficient for the cotton transition; and $Temp$ is the PET annealing temperature.

Similarly, taking the gradient of plots of Figs 5 and 6, we have respectively,

$$(C_{\text{Coeff}}^{\text{PET}}) dB = dY_{\text{PET}} \quad (6)$$

$$(T_{\text{Coeff}}^{\text{PET}}) dTemp = dY_{\text{PET}} \quad (7)$$

where dB is the change in the PET component in the PET/cotton blend,

$T_{\text{Coeff}}^{\text{PET}}$ is the thermal coefficient due to the PET, and $Temp$ is the PET annealing temperature.

Equations 4, 5, 6 and 7 indicate that, while the blend composition seems to increase with the peak area, the effect of annealing seems to cause a reduction in the magnitude of the ultimate peak area. Equations 4, 5, 6 and 7 could be written respectively as:

$$(C_{\text{Coeff}}^{\text{Cot}}) A = Y_{\text{Cot}} \quad (9)$$

$$(T_{\text{Coeff}}^{\text{Cot}}) Temp = - Y \quad (10)$$

where A is the cotton component in the PET/cotton blend, and

$$(C_{\text{Coeff}}^{\text{PET}}) B = Y'_{\text{PET}} \quad (11)$$

$$(T_{\text{Coeff}}^{\text{PET}}) Temp = - Y' \quad (12)$$

where B is the PET component in the PET/cotton blend. Equations 9, 10, 11 and 12 give information about the various interactions involved in the cotton and PET transitions, that is, the cotton fraction and the corresponding PET fraction positively influence their respective peak areas, while the previous thermal history contributes a lowering effect on their peak areas and hence their transition energies. These interactions could be in the form of:

(1) some kind of cross-linking facilitated at elevated temperatures, such as suggested by Landel [5] for the polyisobutylene-glass bead system;

(2) Van der Waals forces of attraction between cotton and PET, cotton and PET-PET; it is noted that because of the pulverization procedure employed, a large surface area for PET and cotton is generated, which facilitates a high degree of cotton-PET contact;

(3) the degree of crystallinity of the PET, caused by its previous thermal history.

References

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RÉSUMÉ — Les courbes DSC des combinaisons polyester/coton indiquent que la température de transition vitreuse T_g du coton varie avec la composition. On présente des courbes types pour le contrôle de la qualité d'après les surfaces des pics de transition du coton ou du PET. On a déterminé les facteurs qui influencent la dimension des surfaces des pics: l'un est en rapport avec la composition et l'autre avec le coefficient thermique.

ZUSAMMENFASSUNG — Die DSC-Kurven von Polyester/Baumwoll-Gemischen zeigen, dass die Glas-Übergangstemperatur (T_g) der Baumwolle sich mit der Zusammensetzung des Gemisches ändert. Standardkurven für Qualitätskontrollen werden gezeigt, welche auf den Übergangspeakflächen der Baumwolle oder des PETs beruhen. Die zur Größe der Peakfläche beitragenden Faktoren wurden bestimmt: ein Zusammensetzungskoeffizient und ein thermischer Koeffizient.

Резюме — ДСК-кривые смесей полиэфира и хлопка показали, что температура перехода T_g хлопка в стеклообразное состояние изменяется с изменением состава смеси. Для качественного контроля представлены стандартные кривые, которые определены на основе площади пиков хлопка или полиэфира. Установлены фактор состава и термический фактор, определяющие величину площади пиков.