

THE EFFECT OF COPOLYMERIZATION ON TRANSITION TEMPERATURES OF POLYMERIC MATERIALS

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Abstract

The relationship between transition temperatures and copolymer composition was studied by DSC. Three types of copolymers were studied: styrene-acrylonitrile (SAN), vinyl chloride-vinyl acetate (VC-VA), and ethylene vinyl acetate (EVA). SAN's and VC-VA's are amorphous copolymers, whereas EVA's are semi-crystalline copolymers. The variation of the glass transitions and the crystalline melting are discussed in this study.

Keywords: copolymers, transition temperatures

Experimental

A Shimadzu DSC 50 calorimeter was used to measure the transition temperatures.

An initial run with controlled heating and cooling was performed in order to assure equivalent thermal history in all the samples. The conditions used on the preliminary thermal cycle were different for each material studied, depending on the polymer type and temperature of the transition. They will be given below in separate sections.

Samples of copolymers with different percentage compositions were analysed and their relative compositions were confirmed by infrared spectrum analysis.

The results that will be given below in separate sections were obtained as the mean value of five runs for each sample. The maximum difference between runs of the same sample was 1°C.

Styrene-acrylonitrile copolymers

Three different percentage compositions of SAN copolymers were studied in DSC: 20% AN, 25% AN, and 30% AN.

The conditioning run applied to these samples was: 20°C min⁻¹ heating rate until 180°C, 10 min at 180°C, and -10°C min⁻¹ cooling rate until 30°C, with a nitrogen flow of 20 ml min⁻¹. The analytical conditions were: 20°C min⁻¹ heating rate, until 180°C with the same N₂ flow.

Material	PS	SAN			PAN
		20% AN	25% AN	30% AN	
T_g /(°C)	106	107	109	110	106

The glass transition temperatures obtained for the copolymer SAN were compared with the values measured for the corresponding homopolymers: PS and PAN.

We noticed that:

- The glass transition temperatures of the copolymers are slightly higher than those of the two homopolymers, and
- The glass transition temperatures for the copolymers appear to increase slightly as the AN content is raised.

However, the increase in T_g with increasing of AN content is very small, and it is within the error of the method of measurement. The copolymeric effect on glass transition can be realized because the two homopolymers, PS and PAN have identical glass transition temperatures.

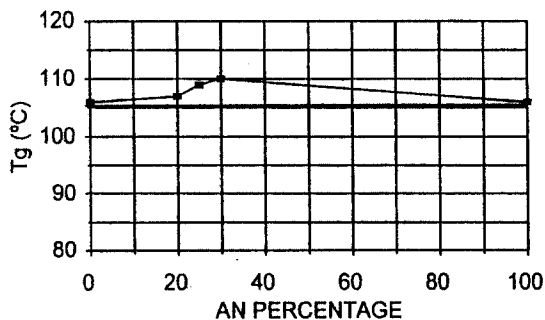


Fig. 1 Relation between acrylonitrile percentage in SAN copolymers and glass transition temperatures

The effect is shown in Fig. 1.

The glass transition temperature of a random copolymer usually falls between those of the corresponding homopolymers, as copolymers tend to have intermediate chain stiffness and interchain attraction [1]. In the case of this study, the T_g of the two homopolymers are identical and that for the copolymer is found slightly higher. Hydrogen bonding or dipole attraction can occur between different comonomer constituents and not between similar constituents.

Vinyl chloride-vinyl acetate copolymers

Four different percentage compositions of VC/VA copolymers were studied: 2.5% VA, 10% VA, 13% VA, and 17% VA.

The conditioning run applied to these samples was: 20°C min⁻¹ heating rate until 130°C, 10 min at 130°C, and -10°C min⁻¹ cooling rate until 0°C, with a nitrogen flow of

20 ml min⁻¹. The analytical conditions were: 20°C min⁻¹ heating rate, until 130°C, with the same N₂ flow.

Material	PVC	2.5% VA	10% VA	13% VA	17% VA	PVA
$T_g/^\circ\text{C}$	87	87	80	71	77	35

The T_g values obtained for the copolymers were compared with those for the corresponding homopolymers below:

The transition temperatures for the VC/VA copolymers fall between the T_g s of the corresponding homopolymers.

As the VA percentage increased from 2.5% to 17%, the copolymers T_g decreased monotonically. The slight dip of T_g at 13% VA is not understood; however

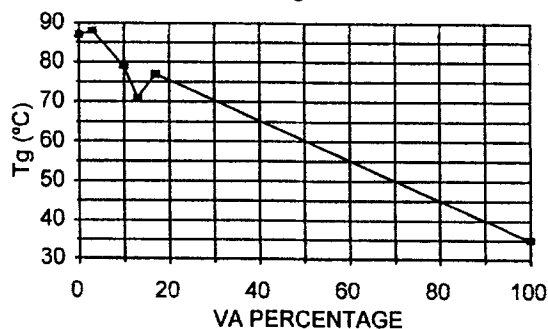


Fig. 2 Relation between vinyl acetate percentage in VC/VA copolymers and the glass transition temperature

it is clear that the incorporation of VA content lowers the T_g of PVC. The T_g vs. composition is shown in Fig. 2.

In the case of VC/VA copolymers we see an almost linear relationship between the glass transition temperatures and the composition. This is commonly seen when chain stiffness and interchain attraction are the only important factors to be considered [1]. There is a deviation from a linear relationship at 13% VA content. The explanation for this effect requires a more detailed study of the molecular weight, possible long branching chains, and sequence distribution, which are factors that could affect the T_g value and were not determined in this study.

Ethylene-vinyl-acetate copolymers

Five samples with different percentage compositions of EVA were studied: 14% VA, 18% VA, 25% VA, 28% VA, and 33% VA.

The conditioning run applied to these samples was: 10°C min⁻¹ heating rate until 140°C, 10 min at 140°C, and -10°C min⁻¹ cooling rate until 30°C, with a nitrogen flow of 20 ml min⁻¹. The analytical conditions were: 10°C min⁻¹ heating rate, until 140°C with the same nitrogen flow.

The crystalline melting points measured for the copolymers were compared with that for the low density polyethylene. The T_m for polyvinyl acetate was not measured.

Material	Polyethylene	EVA				
		14% VA	18% VA	25% VA	28% VA	33% VA
$T_m / ^\circ\text{C}$	120	90	87	72	71	65

The melting points are compared below:

The crystalline melting points of EVA decreased when the vinyl acetate percentage is increased. The VA branch points interrupt the crystallization of polyethylene chains, thus affect the perfection of the crystallization and melting points.

The melting points vs. composition of the EVA's are shown in Fig. 3.

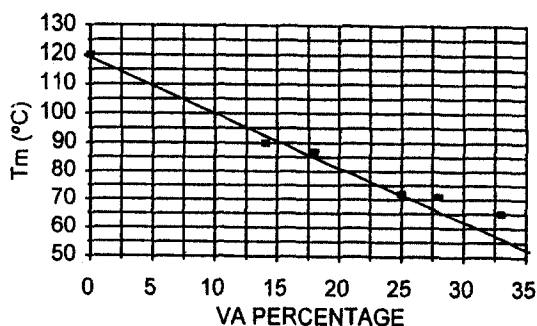


Fig. 3 Relation between vinyl acetate percentage in EVA copolymers and crystalline melting point

The crystalline melting points of EVA copolymers vary with composition. The linear relation observed for the range of study shows a link between thermal behavior and percentage composition. This makes the use of the T_m measurement a good procedure for preliminary characterization of EVA copolymers.

References

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