



# The mechanical behaviour of ZnO nano-particle modified styrene acrylonitrile copolymers



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## ABSTRACT

Two amorphous SAN copolymers with acrylonitrile contents of 24% and 34% have been modified by the incorporation of ZnO nano-particles at volume fractions of up to 2.00%. For the SAN with 24% acrylonitrile content, three types of nano-particles were added. The first two were cylindrical (nano-rods) and the third were spherical. For the SAN with 34% acrylonitrile content, just one of the cylindrical nano-particle types were used. The dispersion of the nano-particles was assessed using atomic force microscopy and agglomeration was observed for the higher volume fractions. Young's modulus and fracture toughness values were measured for each system as a function of volume fraction. The smaller nano-rods were found to be the most effective for both stiffening and toughening the polymers and the spherical particles were found not to contribute to stiffness due to poor particle–matrix adhesion. At room temperature the maximum toughening contributions for all particles occurred at volume fractions of about 0.1%, above which a reduction was observed. At 80 °C the toughening contributions continued to rise slowly past 0.1% volume fraction. The toughening is consistent with the notion that the particles debond from the matrix and then plastic hole growth around the detached particles is initiated. The peak toughening observed at 0.1% volume fractions are the result of agglomeration occurring at higher volume fractions.

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## 1. Introduction

In recent years the modification of polymer properties via the incorporation of nano-particles has been a very popular research topic. Much of the literature has focused on the addition of spherical nano-particles to thermosetting matrices [1–3], where relatively large quantities of particles can be well dispersed, without agglomeration occurring. Typically it is more difficult to disperse nano-particles into thermoplastic matrices. Extrusion mixers and particle surface treatments are widely used techniques to facilitate this process [4]. However, agglomeration of nano-particles remains a problem in thermoplastics at relatively low particle volume fractions and thus efforts continue in the field to improve this situation. The use of different particle shapes and aspect ratios can have an effect on dispersion, for example spherical particles may be replaced with cylindrical, rod-like particles of various diameters and aspect ratios, and there has been much interest also in the use of carbon nano-tubes [5].

Once the nano-particles are dispersed into the polymer matrix, many researchers have reported that significant stiffening and toughening can occur. The stiffening requires load transfer to take place between the relatively low Young's modulus polymer matrix and the usually much higher Young's modulus particles. The simple rule of mixtures can then be used to predict the resulting Young's modulus of the nano-composite. Although there are complications (e.g. aspect ratio and orientation effects and the potential agglomeration of particles) the basic mechanism for stiffening is well understood. However, a universally accepted explanation for the improved toughness values is currently lacking. Workers have identified a number of mechanisms that contribute to the toughness of nano-composites and efforts have been made to determine their individual contributions and also their combined effects. The toughening mechanisms that have been proposed include particle–matrix debonding, the subsequent plastic void growth [6], shear yielding (or shear banding) of the matrix between the particles [1,7], and in some cases crack tip bridging [5] (e.g. when nano-tubes are employed). Also, more recently workers have employed a multiscale modelling strategy to describe the toughening of polymers by nanofillers with different properties being ascribed to the matrix and interphase regions

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around particles [8–10]. Such work has considered the combined effects of debonding, plastic yielding of nano-voids and shear banding in the polymer matrix [10]. The model proposed in [6] to describe debonding followed by plastic void growth has been used to determine the energy density of matrix shells around debonding particles using a geometrical description of particle–particle interactions [11,12].

In the present work, two thermoplastic copolymers SAN with 24% acrylonitrile and SAN with 34% acrylonitrile were modified with three different nano-particle types - two rod-like, cylindrical particle types and spherical particles. The enhancements in stiffness and toughness have been measured experimentally in a series of tests at 23 °C and 80 °C.

The model proposed in [6] to describe nano-composite toughening enhancement due to the addition of spherical particles by (i) particle–matrix debonding followed by (ii) plastic void growth was extended to accommodate toughening with nano-rods and nano-tubes [13]. Here experimental data for SAN toughened with nano-spheres is analysed using the spherical model [6], and also SAN toughened with two sizes of nano-rods are analysed using the analogous model for rod-like particles [13]. The models define a toughness enhancement factor,  $X$ , which is determined from experiment (for either spheres or rods). The measured values of  $X$  (up to the limiting volume fraction when agglomeration occurs) have been used to determine the model parameters  $G_d$  (the energy for debonding) and the critical interfacial stress,  $\sigma_c$ , which controls the subsequent plastic void growth from the debonded particle.

## 2. Materials

Two grades of amorphous SAN copolymers were used in this study. The first had a trade name of Luran VLN and contained 24% acrylonitrile in the copolymer. This is referred to as SAN-24 in the present work. The second had a trade name of Luran VLP and contained 34% acrylonitrile in the copolymer. This is referred to as SAN-34 in the present work.

Three types of ZnO nano-particles were employed as fillers, denoted here as Types A, B and C. Types A and B were nano-rods and Type C were nano-spheres. Type-A nano-rods had an average diameter of 40 nm with an aspect ratio (length/diameter) of 4, Type-B nano-rods had an average particle diameter of 12 nm with an aspect ratio of 3, and Type-C particles were spherical with an average diameter of 10 nm. All materials were supplied by BASF SE, Germany. The dimensions of the particles are summarised in Table 1.

The particles were surface modified with trioxadecanoic acid (TODS) or with one of two different types of silane before blending in order to improve the dispersion of the particles into the matrix. The SAN and ZnO blends were compounded in a Werner & Pfleiderer ZSK-30 twin screw extruder and the melt was extruded through a flat sheet die. Prior to compression moulding, the raw sheets were dried at 80 °C in vacuum for 36 h. The resulting sheets were then compression moulded into 6 mm and 4 mm thick plates using a hot compression moulding machine (DAKE, USA) at 200 °C and 5 MPa. The composite systems studied are listed in Table 2.

Concerning the nomenclature used in the present paper, when nano-particles are added to the system, the volume fraction of particles is shown in the system designation preceding the particle

**Table 1**  
Details of the ZnO nano-particles used.

Particle designation	Shape	Diameter (nm)	Aspect ratio (l/d)
A	Nano-rod	40	4
B	Nano-rod	12	3
C	Nano-sphere	10	1

**Table 2**

The nano-composite systems studied and testing temperatures.

Matrix; particles→	"Composite designation" and (test temperatures)		
	A	B	C
SAN-24	"SAN-24-A" (23 °C)	"SAN-24-B" (23 °C & 80 °C)	"SAN-24-C" (23 °C)
SAN-34	-	"SAN-34-B" (23 °C & 80 °C)	-

Note: (-) indicates not tested.

type, e.g. system "SAN-24-0.5A" contains 0.5% by volume fraction of Type-A particles. As will be discussed in the next section, for systems modified with the Type-B particles, tests were performed at two temperatures; namely 23 °C and 80 °C.

## 3. Experimental

### 3.1. Thermal analysis

The thermal behaviour of the unmodified and particle modified composites was studied via dynamic mechanical thermal analysis (DMTA). Tests were performed on bars of dimensions  $50 \times 3 \times 2$  mm in a 'PerkinElmer DMA 8000' apparatus. Dual cantilever geometry was employed, at two different frequencies of 1 Hz and 10 Hz over a temperature range from 20 °C to 140 °C. At least two specimens were tested for each formulation, and the  $T_g$  was defined to be the temperature at the peak value of the loss factor,  $\tan \delta$ , as specified in the ISO standard [14].

### 3.2. Microscopy

To investigate the particle dispersion in the various systems, atomic force microscopy (AFM) analysis was undertaken using a 'MultiMode' scanning probe microscope from Veeco (Santa Barbara, USA) equipped with a 'J' scanner and a 'NanoScope IV' controller. A smooth surface was first prepared by cutting the samples on a 'cryo-ultramicrotome' at 23 °C. The scans were performed in tapping mode using etched silicon probes supplied by Veeco and both height and phase images were recorded simultaneously.

To allow an investigation of the fracture surfaces following fracture testing, a 'Hitachi S-3400 N VP' scanning electron microscope was used. Typically, an accelerating voltage of 15 kV was used, and the working distance was approximately 10 mm. The fracture surfaces were sputter coated with a very thin layer of gold (about 15 nm thick) to reduce charging effects prior to the SEM examinations. The SEM images could show the morphology of the specimens, and also the roughness of the fracture surface and the fracture path.

### 3.3. Tension, compression and fracture testing

Specimens for testing were prepared in both the longitudinal and transverse directions on the mouldings with respect to the previous direction of extrusion and no effects of orientation were observed in the results. Tensile tests were performed on an Instron testing machine (model 5584) running Bluehill™ control software. The tests were conducted in accordance to ISO 527 [15] standards to determine the Young's modulus. *E*. Dumbbell samples, approximately 4 mm wide  $\times$  4 mm thick were used. At least five specimens were tested for each formulation. All tests were performed using a contact extensometer with a gauge length of 25 mm, at a crosshead speed of 1 mm/min.

Uniaxial compression tests were performed to determine the yield stress,  $\sigma_y$ , since testing of relatively brittle materials such

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