

MOLECULAR ORIENTATION IN COMPOSITES

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ABSTRACT

The idea of this work is to use the molecular orientation in composites aiming to improve the state of dispersion of nanoparticles in polymeric matrices. This molecular orientation in composites like Polyvinylchloride (PVC) with addiction of calcium carbonate are used mainly in fibers and film with self-reinforcement in several applications applied in pipes for high pressure pumping. The anisotropy in the composite induced by different orientation ratios can cause several changes in the material properties. Techniques like Wide Angle X-ray (WAXS) showed clearly that the organization in the material has changed. In addition, tensile tests, nanoindentation analyses and density tests showed significantly reductions in the hardness and density with the increase ratio of orientation. Although FT-IR indicated no differences in the chemical structure during the process of mechanical orientation.

Keywords: molecular orientation, polymers, composites, PVC

INTRODUCTION

Polyvinyl chloride (PVC) is one of most used thermoplastics in industry. In many cases PVC is mixed with Calcium carbonate to improve the process window and to reduce the material costs. PVC is commonly known with very low crystallinity from 5 - 10% that influence significantly the process and the mechanical properties, but this range can reach values greater than 30%. During the 60's and 70's of XX century has begun the development of technology to orient PVC to increase the mechanical properties. The orientation process and the organization in the material is added with a mesomorphic structure to the crystallinity. Kim and Gilbert⁽¹⁾ analyzed these structures with the X-ray diffraction where in oriented PVC fibers could be identified the mesomorphic structure.

MATERIALS AND METHODS

The PVC grade used was a compound, where the PVC had a k-value of 67 (NBR 13160), Calcium carbonate, stabilizer and pigment were added in a mixer Plasmec 1000l where the temperature reached 120°C and then it is cooled down to 60°C. After a two days conditioning at room temperature the compound was extruded to a pipe with a Battenfeld extruder BEX 90-22. This pipe was cut in stripes

for the stretching part. Then these stripes were heated up to 100°C for 10 min and stretched with different draw ratios (DR) by constant drawing speed (200mm/min). The stretching process were fixed based on the work of Hitt and Gilbert⁽²⁾. These DR were analyzed from DR=1 undrawn, to 1.5, 2.0, 3.0 and 3,5. The drawing process was hold until the samples reach temperatures above the glass temperature. From the stretched parts of the stripes were got the samples that have been analyzed in different tests.

For the tensile test to obtain more accurate results for the stretched PVC compound, dog bonetype specimens were drilled with dimensions of 19 x 115 mm (width x length) in the middle section to standard samples of the ASTM 0638 Standard type IV. For the nanoindentation was used a Nanoindenter XP device with a Berkovich indenter. With the method of Oliver and Pharr were measured the Young's modulus and the nano hardness in eight indentations samples. A maximum load of 50mN was used with nine cycles of loading and unloading in each indentation. The X-ray analyze was carried out by a Bruker X-ray diffractometer with traces from $5 - 90^{\circ}$ of 2θ using step size of 0,02°.

To analyze the tensile properties like it mentioned before were used a EMIC unidirectional tensile test equipment with extensometers and a script of the ASTM 0638 Standard Test Method for Tensile Properties of Plastics. Eight samples of each drawing ratio were tested uniaxial in draw direction with a speed of 5mm/min. The electron microscopy laboratory has a Zeiss scanning electron microscope, to which an EDX microanalysis system is attached. The equipment allows the superficial characterization of the materials. For sample preparation, an evaporator is used that allows the deposition of thin layers of gold or carbon. To confirm no material changings were tested also drawn and undrawn samples with thermogravimetric analyze (TGA) with a TA Instruments Q500. FTIR spectra of the compound were analyzed by a Perkin-Elmer Spectrum One B spectrophotometer.

RESULTS AND DISCUSSION

The results of the experimental work showed in WAXS indicated that the nanoscopic structure of the PVC change significantly with the ratio of orientation of the material. On small angles i.e. 20 around 9° the material organizations have a great difference between the high oriented to the non-oriented compound, like it can be seen in Figure 1. This kind of peak at low angles is a clear sign of reorganization in the material at nanoscale.



Figure 1 – X-ray diffraction with and without orientation.

Furthermore , the results of tensile properties, as presented in Figure 2 and Table 1 indicated reinforcement in the mechanical properties of the materials.



Figure 2 - Tensile stress with different DR

The numerical values indicated that modulus and tensile strength increased according to the draw ratio increased. In addition the results clear indicated that reinforcement is achieved and the more stretched the material smaller the elongation at break.

Table 1 – Tensile properties with different DR.				
Draw ratio (%)	Tensile strength (MPa)	Modulus of elasticity (MPa)	Elongation at break (%)	
100%	41.559	3.351	103,6	
150%	56.422	4.430	34,7	
200%	78.578	4.872	20,8	
250%	91.844	5.472	12,2	

In figure 3 FTIR showed no differences between the stretched and unstretched samples. It can be said that the difference in the properties are caused by physical alignments of the molecular chains of the composite. For simplicity it is presented below in figure 3 FT-IR analyses of similar spectra of undrawn and 300% DR stretched samples.



Figure 3 – FT-IR spectrometer with and without orientation

The thermal degradation of the different samples has the same start temperature and small differences after that in their profile as presented in figure 4.



Figure 4 – TGA spectrometer with and without orientation

CONCLUSIONS

In this work the applied molecular orientation was successful inducing nanoscopic structure in a material that is expected to be amorphous. These structures are responsible for reinforced the mechanical properties up to 100% in tensile strength and 63% in modulus of elasticity. FTIR analyses showed that no shoulders or new bands are presented in the stretched material when compared to the neat resin. In addition TGA showed any substantial changes in thermal degradation between all samples. In future work it is expected to applied this technique of molecular orientation to improve the state of nanofillers in nanocomposites.

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