Composites based on carboxylated Poly(styrene-co-butadiene) Reinforced with Kaolin Fillers as Studied by Dynamic Mechanical Analysis

J.A. Trejo-O´Reilly[1], A.Hernández-Hernández[1], C. Dichtel[2] and. J.Y. Cavaillé[2]

[1)] Centro de Investigación y Desarrollo Tecnológico (CID), S.A. de C.V, Av. de los Sauces 87. Mza 6. Parque Industrial Lerma , Edo. de México C.P 52000, México. Fax (52 728) 528-99. Email: jatrejo@mail.girsa.com.mx
[2)] Groupe d'Etudes de Métallurgie Physique et Physique des Matériaux, UMR CNRS-INSA #5510, INSA de LYON, F-69621 Villeurbanne cedex, France. Email: cavaille@insa-lyon.fr

SUMMARY: Composite materials were made with styrene / butadiene latex and kaolin fillers in aqueous suspensions. The mechanical properties of the different composite materials were measured with a dynamic mechanical analyzer using a cantilever geometry at 1 Hz in the temperature range [-120°C, 120°C]. The fillers vol% was chosen between 0 and 36 (up to 90 w%). The maximum filler amount was limited to about 36 vol% due to the too high brittleness of the materials obtained above this value. The Halpin-Kardos (HK) equation will have to be modified to account for the viscoelastic behavior of the composite material above the percolation threshold as expected from previous works. The HK equation underestimates the storage modulus. In order to quantify the deviation from experimental data, an adjustable parameter should be included. However, the mechanical response of these composite materials did not follow a classical percolation theory where the particles are supposed to form a rigid skeleton. In this case, the increment of stiffness comes from a flexible skeleton of particles in contact, but without moment transfer.

Introduction

Poly(styrene-co-butadiene) (PSB) carboxilated emulsion polymers are largely used for technological application (as paper coating, etc.). A better knowledge of their specific interaction with fillers such as kaolin, calcium carbonate or TiO_2 is required [1]. Some of the most important features of coated paper are opacity, brightness, porosity, surface cohesion, printability, surface strength (dry pick), etc.[2,3] These interactions are very specific according to the type of paper used (acid or basic paper formulation during its manufacture). The polymer structure (particle diameter, gel content, Tg, etc.) as well as the type of filler, the machine for coated paper, the drying variables, etc., all are very important in order to achieve

 CCC 1022-1360/00/$ 17.50+.50/0

the desired properties. This work is focused on systems obtained from the mixture of a carboxilated styrene-co-butadiene copolymer (latex) and kaolin particles dispersed in water (kaolin slurry). Films obtained after evaporation of water are studied and considered as composite material. We used the Halpin-Kardos (HK) equation to predict the viscoelastic response of the samples. The reason for the discrepancy between experimental and calculated data is discussed as a consequence of interactions between fillers as their volume fraction can reach high values.

Experimental

In order to better understand the complex interactions in the paper coating formulation, our experimental approach was to make composite materials starting with a typical poly(styrene-co-butadiene) carboxilated latex with a solid content of 52 w%, average particle diameter of 188 nm., and pH equal to 7.5. After its extraction from toluene, the polymer had a gel content of 85%. Kaolin fillers are available as aqueous suspension with a solid fraction of about 30 vol%. The composite materials were made by slowly adding the slurry to the latex with mild mixing (with a shear rate enough to mix but not too high to provoke air bubbles formation). The polymer / filler volume ratio was chosen from 100/0 to 64/36 (0, 4, 10, 16, 20, 28, 32, 36 vol%). Due to their high brittleness above the latter level (36 vol.%), the materials were not further studied. In order to prepare the different composite materials for the mechanical measurements, specimens were cast thin layer by thin layer with a drying step each time, to limit the effect of sedimentation. Each layer had a thickness around 0.2 mm. The thickness of final samples was around 3 mm., with a length of 33 mm. and 6 mm in width. The drying conditions were 25ºC for one week, 50ºC for 48 hours and at 110ºC for 30 minutes.

Synthesis

Emulsion polymerization of S/B carboxilated latex was made according to standard industrial procedures in semicontinuous conditions. The ratio used of styrene / butadiene latex for this study was 50/50 in weight.

Characterization

Polymer

Monomer conversion of the reactions was determined gravimetrically. The gel content in the latex particles was done following the ASTM-1417-90 method. Particle size was determined using dynamic light scattering (Horiba LA-910) The result in volume analysis is a mean diameter of 0.188 μm, a standard deviation of 0.046 μm and a measured specific area of 335776 cm^2/cm^3. DSC experiments were performed to characterize the latex polymer with a DSC 101 Setaram model, with typical sample weight of 15 mg. The polymers Tg was around -5°C Samples were run from -100 to 100°C. The dynamical mechanical analyzer (DMA) worked in single cantilever mode, at 1 Hz, at a heating rate of 3°C/min, with a maximum amplitude of 20 μm, in the temperature range [-120°C to 120°C]. The DMA setup used is a TA 2980 model (from TA Instruments).

Fillers

The average size of fillers was around 1 μm from TEM observations, but it is clearly visible that they have a platelet aspect. We can see from Figure 1, that their regular shape is hexagonal and that they are quite polydispersed. The size distribution was characterized using a Horiba LA-910 light scattering analyzer. The result in volume analysis is a mean diameter of 1.55 μm, a standard deviation of 0.56 μm and a measured specific area of 44221 cm^2/cm^3.

Mechanical coupling modeling

Classical models for taking into account the reinforcing effect of rigid fillers dispersed in a soft matrix are based on the calculation of the stress transfer from the matrix towards the fillers. As it is impossible to perform the exact calculation in the case where the fillers are close each other, it is classical to use homogenization technique within a mean field approximation. Among these approaches, it exists numerical methods and few analytical equations, easier to use and already widely tested. Among them, the HK equation [4], has

been initially derived for semi-crystalline polymers, but was also used for polymeric matrix reinforced with short fibers as fillers. The analytical calculation was derived considering the samples as laminates made of four oriented plies (0°, -45°, +45°, 90°). The modulus of each ply, E_{ii}, where i refers to the longitudinal direction (i=1) or transversal (i=2) of fillers, is:

$$\frac{E_{ii}}{E_m} = \frac{2E_{ii}(1+\nu_m)(1+\xi_{ii}X_f) + 4\xi_{ii}(1+\nu_m)^2(1-X_f)G_m}{E_{ifi}(1-X_f) + 2(\xi_{ii}+X_f)(1+\nu_m)G_m}$$

$$\frac{G_{12}}{G_m} = \frac{G_f(1+\xi_{12}X_f) + \xi_{12}(1-X_f)G_m}{G_{ifi}(1-X_f) + (\xi_{ii}+X_f)G_m}$$

where E_{iif} is the Young modulus in the filler direction i (i=1,2). G_f and G_m are the shear moduli of the filler and matrix, respectively, ν_m is the Poisson's ratio of the matrix and X_f is the volume fraction of fillers. The aspect ratios, ξ_{ii}, are defined as follows:

$$\xi_{11} = 2\left(\frac{L}{e}\right); \xi_{22} = 2\left(\frac{l}{e}\right); \xi_{12} = \left(\frac{l}{e}\right)^3$$

where L, l and e are the length, the width and the thickness of the fillers, respectively.

The shear modulus of the composite can be written as follows:

$$G = \frac{E_{11} + E_{22}(1-\nu_{12})}{8(1-\nu_{12}\nu_{21})} + \frac{G_{12}}{2}$$

where $\nu_{12} = X_f\nu_f + (1\text{-}X_f)\nu_m$, and $\nu_{21} = \nu_{12}\frac{E_{22}}{E_{11}}$

Results and Discussion

The wettability and the adhesion between polymer and filler are induced by i) using a very low surface tension agent in the synthesis of the latex, ii) a highly carboxilated polymer particles surface and iii) use of kaolin in slurry type. The wide particle size kaolin filler distribution is a positive aspect in order to obtain a better dispersion in the final dried composite material. Indeed, the interfacial analysis of the adhesion between polymer and filler should be studied but will be part of further publications as well as the morphological studies of the filled films. The exact values of storage and loss modulus of the different materials are difficult to obtain in the single cantilever arrangement because it is experimentally very difficult to have perfect samples with very regular dimensions. This is the main reason to use relative modulus, which have been proven to be very accurate based on several previous works [5,6,7]. It was assumed that at low temperature, i.e. when the matrix is very stiff, the

HK equation applies. Figure 2 exhibits the storage modulus (log scale) versus temperature for all the filler compositions. It appears that above Tg, the reinforcing effect increases more rapidly than for the expected amount of fillers as compared with the HK equation and all mean field mechanical coupling calculation. For these calculations, the values of the parameters were (where *f* refers to as for the filler and m for the matrix): E'_m and E''_m come from experimental data; the fillers modulus cannot be determined but have been estimated and maintained constant: $G'_f = 5.10^9$ Pa, $E'_{11f} = 15.10^9$ Pa, $E'_{22f} = 15.10^9$ Pa, $E''_{11f} << E'_{11f}$; $E''_{22f} << E'_{22f}$ and $G''_f << G'_f$; $L = 1$ µm, $l = 0.5$ µm, $e = 0.3$ µm. The kaolin density was 2.5 (g/cm^3). The loss modulus (E'' or G'') have been considered to be negligible in comparison with the storage modulus (G', E'). Due to the thermal stability of the fillers, their mechanical properties were kept constant during the whole test cycle. Figure 3 shows the storage modulus measured at 70°C, i.e. well above Tg of the matrix, versus the filler content, and for comparison the predicted data from the HK equation. It is clear that below 10 vol.% the agreement between calculations and experimental data is rather good, but above this level the HK equation underestimates the experimental modulus. These kinds of results have already been previously observed [5,6,7], and come from an additional reinforcing effect which arises when stiff fillers form a network. This confirms that for aspect ratio higher than one, the threshold for percolation is lower than 20 vol.% (close to the generally accepted fraction for percolation of randomly dispersed spheres).

Fig. 1. TEM of kaolin fillers.

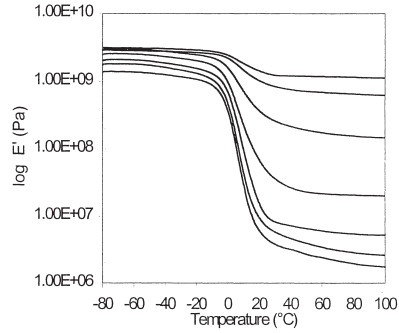

Fig. 2. Experimental results of DMA composite Materials having different filler %-volume (0, 4, 10, 20, 28, 32 and 36%-v).

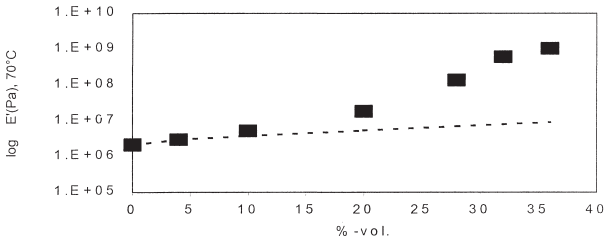

Fig. 3. (–) Halpin-Kardos model and ◆ Experimental data

Conclusions

The study of the mechanical properties of paper coating material was performed on bulk composite materials prepared from a mixture of poly(styrene -co- butadiene) latex and a kaolin slurry. The main result is that at increasing fraction of kaolin, the stiffness of this composite material increases much more than expected from classical mean field approach calculation. It appears that above 10 vol.-% of kaolin particles, their percolation should be responsible for this discrepancy. The latter is consistent with their aspect ratio close to 0.3 define as the thickness divided by the average diameter. In addition, it is not sure that these particles are randomly dispersed, and they could agglomerate in such a way that they percolate at a smaller threshold than the theoretical one. The consequence of such a situation is the formation of a more or less flexible network, which is much more efficient than the stress transfer alone from the matrix towards the fillers (which corresponds to the mean field approach).

References

1. M.Y. Boluk and H.P. Schreiber *J. Appl. Polym. Sci.*, **40**, 1783 (1990)
2. J. Watanabe and P. Lepoutre *J. Appl. Polym. Sci.*, **27**, 4207 (1982)
3. R.Hagen,L. Salmen, O Karlsson. and B Wesslen. *J.Appl.Polym.Sci.***62**,1067(1996)
4. J.C Halpin. and J.L Kardos. *J. Appl. Phys.* **43**, 2235-2241 (1972)
5. V. Favier, H. Chanzy and J.Y. Cavaillé *Macromolecules* **28**, 6365 (1995)
6. V.Favier, G.R..Canova,S.C.Schrivastava and J.Y.Cavaillé, *Polym.Eng.Sci.*,**37**,1732 (1997)
7. L. Chazeau, M. Paillet, J.Y. Cavaillé, *J. Polym Sci. Polym. Phys*, *in press*