Effect of Coal on the Rheological and Mechanical Properties of Epoxy Matrix

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Summary : An experimental study was conducted to investigate the effect of coal used as a new type of filler in epoxy networks. For this purpose two series of epoxy composites with different coal weight fraction were studied and their thermo-mechanical properties were characterized. The work demonstrated that coal-filled epoxy networks show a typical behavior of a particulate filled material and follows the theoretical models already used.

Introduction

Epoxy networks are considered as high performance materials, very often used as surface protective coatings, for electronics/electrical applications, composites materials, bonding and adhesives, tooling and castings. Typical fillers used in epoxy networks are calcium carbonate, barium sulfate, talc, kaolin...We proposed to use coal as a new filler in such thermosetting networks. Currently, coal represents an important natural ressource which main use is in the energy field. Coal is a natural substance that has a carbon content between 50 and 98 % [1], and a very heterogeneous structure different from graphite and carbon blacks which have also a high carbon content but a very high density and an ordered structure. Since few years the influence of coal fillers in different epoxy-based networks [2-4] has shown the interest of such systems as compared to other filled materials. The present study focuses on the influence of a high rank polish coal on the rheological behavior and on thermo-mechanical properties of epoxy based networks.

Experimental

Two types of epoxy matrices were synthesized, both are based on Diglycidyl Ether of Bisphenol A (DGEBA, Shell Epon 827, epoxy equivalent weight = 180 g). In the first case the curing agent was novolac (NZ, Sarzyna, Poland, Mn = 570 $g.mol^{-1}$), in the presence of a catalyst, 2-Ethyl 4-Methyl Imidazole (0.3 wt %); in the second case the

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curing agent was diaminodiphenylsulfone (DDS). In both cases the reactants were used as received, the stoechiometric ratio epoxy/OH or epoxy/NH was equal to 1. After fine grinding a high rank coal (Bielzowice, Poland) having the following characteristics: C %wt = 83.6, specific area = 5.5 m^2/g, volatile matter = 27.6%, specific density = 1.331 g/cm^3, particle diameter = 20 to 90 μm, was added after drying to various weight fractions up to 25%. Kinetic of the reaction was studied at 100, 130 and 150 °C using differential scanning calorimetry. Dynamic rheology of the systems was obtained at 100°C in a large range of frequency via a Rheometrics Dynamic Analyser (RDA 700) using parallel plates and the gel time was estimated using different criteria[5]. Fully cured materials were obtained using the following curing cycle: 6 hours at 150 °C for DGEBA/Novolac networks and 6 h at 150°C + 6 h at 200°C for DGEBA/DDS networks. The solid state properties were characterized using dynamic mechanical thermal analysis (TA 2980 instrument), three point bending tests at room temperature and at 110 °C or 180 °C, and fracture toughness measurements with S.E.N samples at room temperature. Morphology was examined using scanning electron microscopy on fracture surface.

Results

Kinetics: The evolution of the conversion versus time is deduced from the value of the residual enthalpy of polymerisation obtained by DSC and is shown in Figure 1 for the neat epoxy/novolac system and for the 16 wt % coal filled system. It can be observed that the crosslinking reaction is very fast: full cure is achieved in less than half an hour at 150 °C. A vitrification phenomena occurs at a curing temperature of 100°C because at this temperature the glass transition temperature of the growing network reaches 100°C. There is no very large difference between the kinetics of the neat and the filled system: at low temperature coal increases slighly the reaction rate. The evolution of the T_g versus the conversion is the same for unfilled and coal filled systems. These results show that this high rank coal which beared only few functional groups (as compared to a low or medium rank coal) is not very reactive towards epoxy functions, as compared to the very fast catalysed epoxy/novolac reaction. The gel time at 100°C was found equal to 30 min using the criterium of the crossover of tanδ curves obtained at different frequencies.

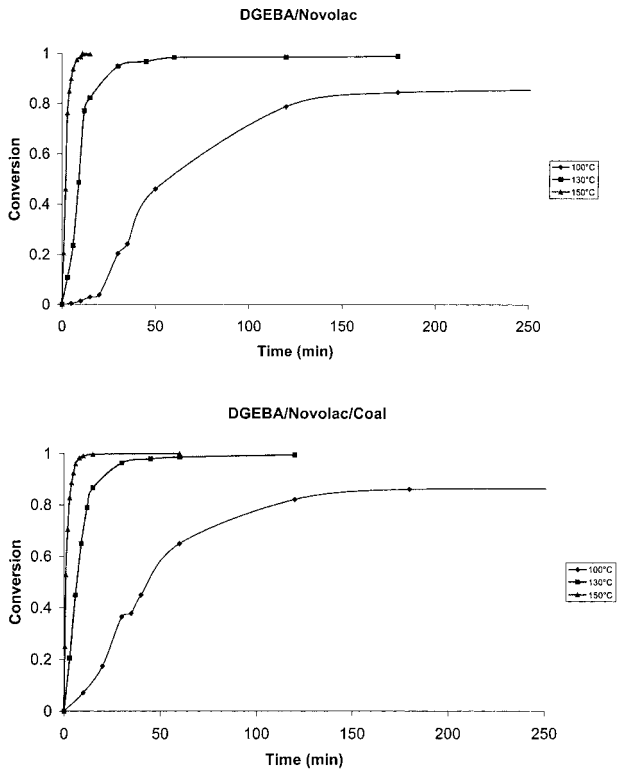

Figure 1 : Variation of the DSC conversion during isothermal cure at 100, 130 and 150°C for neat and 16 wt% coal filled epoxy/novolac systems.

Thermal stability: Coal exhibits a higher thermal stability as compared to other organic fillers like starch, lignin, cellulose, wood. As it can be observed on Figure 2, coal fillers have a strong influence on the thermal stability of the material, especially at high temperature: the weight loss being less as the amount of coal filler is increased.

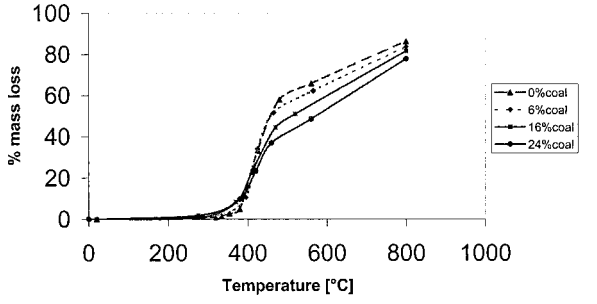

Figure 2: Influence of the coal %wt on the mass loss (10°C/min, under air) in DGEBA/Novolac networks.

Thermo-mechanical properties: Dynamic mechanical spectra are plotted in Figure 3 and show that the temperature at the maximum of tanδ (equal to 148°C for DGEBA/Novolac and 230°C for DGEBA/DDS) is unaffected by the presence of coal fillers. The soluble part of coal[1] does not act as a plasticizier probably because this soluble products bear functional groups able to react with epoxy or amine in such a way that they become link to the network. It is also observed that both the rubbery and the glassy modulus increase with the amount of fillers. Using three point bending tests with unnotched samples, the flexural modulus, E_f, and work at break, W, were recorded. Values of E_f and W are plotted on Figure 4 as a function of the coal wt %, for the two epoxy systems. It can be noticed that DGEBA/Novolac based networks exhibit higher glassy modulus than DGEBA/DDS based networks and that the fillers contribute to an increase of the glassy modulus and to a decrease of the work at break. So, the material becomes more and more brittle as the amount of fillers is increased up to 18 wt%, thereafter properties do not vary significantly. When the test temperature is incresead, a decrease of the modulus and of the work at break is observed for all samples.

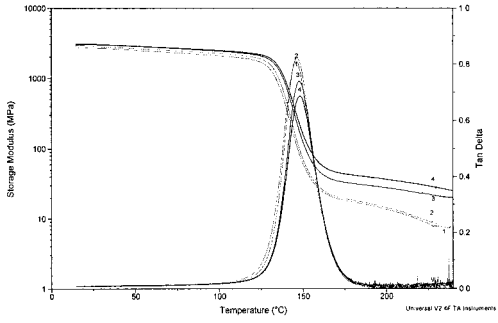

Figure 3: Influence of the coal content on the values of E and tanδ in DGEBA/Novolac networks. 1: 0%, 2: 6%, 3: 16%, 4: 24% coal.

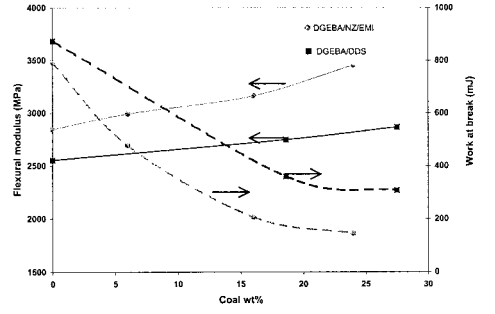

Figure 4 : Variation of the flexural modulus and work at break, measured at room temperature, for the two series of coal filled epoxy networks.

The results from fracture mechanics obtained with notched specimens show that the use of a diamine curing agent, DDS, brings more ductility to the epoxy matrices as compared to the use of novolac. Moreover, higher values of K_{IC} are reached when coal is added up tp 24 wt% to the formulation (from 0.55 $MPa.m^{1/2}$ for neat DGEBA/Novolac system to 0.93 for the 24 wt % coal filled system), following a linear relationship. This result is in agreement with previous results generally obtained with other particulate filled epoxy resins [5]: the fillers are acting as defects but are also reducing the critical stress for crack propagation. Apparent increase in brittleness of unotched samples and increase in K_{IC} at room temperature are not in opposition: as many fillers (glass beads, calcium carbonate...), coal particules are efficient to increase the energy of propagation (crack pinning mechanism) altough they are operating as defects for the crack initiation step. Finaly, the total strenght, taking into account both the crack initiation and propagation steps,was reduced by the presence of filler.

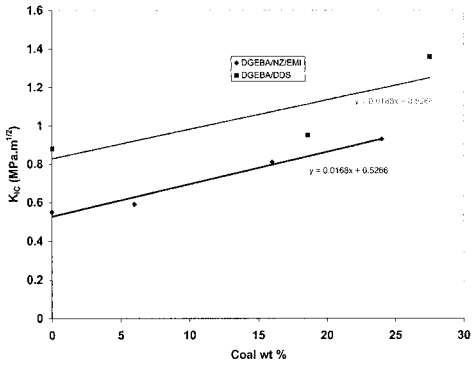

Figure 5: Variation of the stress intensity factor, K_{IC}, at room tempearture for different coal-filled epoxy networks.

Morphology: The micrograph in Figure 6 clearly shows that a good dispersion of coal particles is achieved using our experiemental protocol, the particules have irregular and angular shapes, particle size is found lower than before mixing: it was between 20 and 90 μm, and less than 10 μm after mixing and curing. This is probably due to the effect of the soluble parts initially present in the coal structure, that may dissolved into the epoxy mixture, and it is also associated to the effect of shearing during the blending of components.

Figure 6: Fracture surface of a 18 wt % coal filled DGEBA/DDS network.

Conclusion

It can be concluded that in many ways, coal fillers bring similar properties when added to epoxies as other inorganic fillers (glass beads, calcium carbonate...) or even carbon black or graphite, i.e. increased glassy and rubbery modulus and thermal stability, decrease of the fracture energy and increase in toughness. We have demonstrated the interest of using such fillers for the processing of new filled materials, moreover coal fillers are very cheap. One more advantage is that contrary to most fillers used today that are non-combustible and remain as ash when plastic materials are incinareted, coal has by comparison a very low ash content and provides calorific values..

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