High surface area hyper-cross-linked resins containing GNP or MWCNT

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A synthetic route to produce high surface area polystyrene resins is generally based on the post crosslinking of lightly crosslinked "gel-type" resins obtained by polymerization of styrene (ST) and vinylbenzyl chloride (VBC) in presence of small amounts of divinylbenzene (DVB). The gel-type precursor is usually realized by suspension polymerization, then structural bridges between adjacent phenyl groups are obtained through post cross-linking [1], thus leading to a hypercrosslinked resin (HCLR) characterized by a large microporosity, able to absorb low molecular species, with possible applications for the removal of organic compounds from water or even for hydrogen storage.

In the present study, a new synthetic process was set up, based on the bulk polymerization of the gel-type resin. This method is very interesting for its suitability in large-scale production. In particular, high specific surface area polymers were prepared through extensive cross-linking of a series of gel-type resins, obtained by bulk polymerization of ST, DVB and VBC monomers in different weight ratios.

Moreover, the proposed bulk polymerization also allowed easily incorporating, within the final hypercrosslinked resin, unmodified and surface modified carbon nanofillers, that were found able to modulate the specific surface area and the pore distribution of the materials. In particular, two types of fillers were used: multiwalled carbon nanotubes (MWCNT) and graphite nanoplatelets (GNP).

The distribution of the filler within the polymer was evaluated by TEM analysis on the gel type resins. Furthermore, the extent of the hyper-cross-linking reaction and the structure of the resin were studied by means of FTIR and solid state NMR spectroscopy. The effects of the precursor composition and the MWCNT or GNP content on the surface area of the resins, their pore size distribution and gas sorption capacity were evaluated through nitrogen and hydrogen adsorption analysis. Finally, adsorption tests of phenol were carried out to evaluate the ability of the HCLR and nanocomposites to remove organic contaminants from water.

The realized HCLR showed BET surface area ranging between 450 and 1900 m^2/g as a function of the weight ratio of the monomers. In particular, HCLR resins prepared through the bulk polymerization/hypercrosslinking were characterized by adsorption properties and specific surface area (SSA) values similar to the materials obtained through suspension polymerization/hypercrosslinking, thus confirming that the proposed synthetic protocol is an effective method to realize these high surface area materials.

In the case of HCLR filled with unmodified MWCNT, significant agglomeration phenomena prevented the homogeneous dispersion of the nanofillers within the polymer matrix (see Figure 1a). Therefore, a proper functionalization strategy was set up [2], grafting polyvinylbenzyl chloride (PVBC) on the nanotube surface. As shown in Figure 1b, modified MWCNT (MWCNT-PVBC) showed a very good dispersion within the polymer with respect to unmodified MWCNT. As concerning GNP, an interesting dispersion was already obtained by using the unmodified nanofiller, as shown in Figure 1c.

FTIR and NMR spectroscopy revelead that all the nanofillers did not significantly influence the extent of the hypercrosslinking reaction. Moreover, in the investigated range of compositions, an improvement of surface area, hydrogen adsorption and efficiency of phenol removal from water solution was obtained for the nanocomposite systems containing modified MWCNT and GNP. These results confirmed that well dispersed carbon nanofillers can influence the porosity and the pore size distribution of the hypercrosslinked resins and improve their overall adsorption properties.

References

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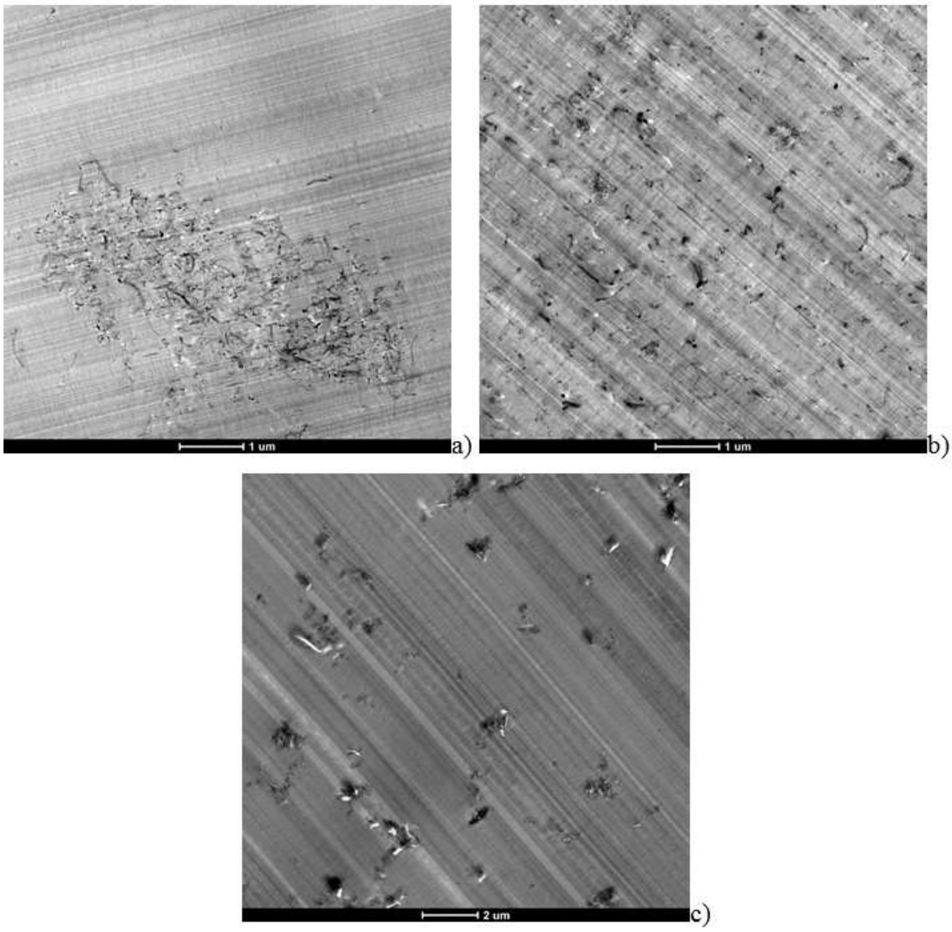

Figure 1. Gel type precursor resin DVB/ST/VBC 2/0/98 containing: a) 3phr of unmodified MWCNT; b) 3phr of MWCNT-PVBC; c) 3phr of GNP.