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European Polymer Journal 42 (2006) 1966–1974
EUROPEAN POLYMER JOURNAL
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Macromolecular Nanotechnology

Synthesis of carbon–polyacrylate nanocomposite materials by crosslinking polymerization

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Received 3 April 2006; accepted 20 May 2006
Available online 10 July 2006

Abstract

Nanocomposite materials made of carbon nanoparticles dispersed in a crosslinked polymer have been produced by light-induced polymerization of a multifunctional acrylic resin containing graphite, oxidized graphite or acetylene black. Exfoliation of graphite was achieved by sonication of the filled resin, and confirmed by sedimentation analysis. Under intense illumination the solvent-free resin was transformed within a fraction of a second into a hard and tough material, at ambient temperature. The photopolymerization was followed by infrared spectroscopy and shown to proceed effectively up to 85% conversion of the acrylate double bonds. The slowing down effect of the carbon particles by screening of the UV-radiation is becoming increasingly important as the sample thickness and the filler content are increased. A redox initiator consisting of benzoyl peroxide and a tertiary amine was used to achieve a deep through-cure of thick samples, a process which was markedly accelerated in presence of acetylene black. These carbon nanocomposite materials proved to be more flexible and resistant to shocks than the neat acrylic polymer. Electrical conductivity was found in nanocomposites containing acetylene black at concentrations above 1 wt.%.

Keywords: UV-curing; Redox polymerization; Acrylates; Carbon black; Nanocomposites

1. Introduction

Nanocomposite polymers have drawn increased attention over the last decade because of their distinct characteristics, in particular superior mechanical and barrier properties, as well as improved thermal stability [1,2]. Most of such composites are made of nanosize mineral particles, like colloid silica, clay platelets or carbon particles, which are dispersed in a polymer matrix. We have recently shown that clay–polymer nanocomposites can be rapidly produced by photoinitiated crosslinking polymerization of multifunctional monomers and oligomers [3–5]. This UV-curing technology offers a number of advantages for the synthesis of nanocomposite polymer materials, namely, an ultrafast polymerization at ambient temperature of

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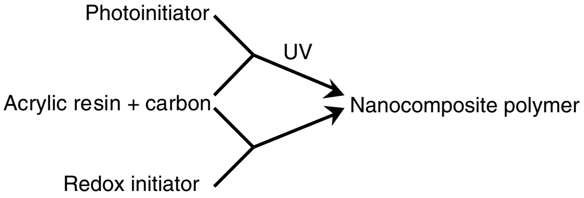
0014-3057/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.eurpolymj.2006.05.027

solvent-free resins with formation of highly resistant polymers. Because of its very low energy consumption and its minor emission of volatile organic compounds, this UV-processing has become specially attractive, given today's increasing concern in the industry for the protection of the environment.

The objective of the present study was to apply the UV-curing technology to the synthesis of polymer nanocomposites containing carbon particles. Because of the important screen effect of this black filler, a dual-curing process combining UV and redox-induced polymerization had to be used in order to achieve a deep through cure of thick specimens. The basic principle can be represented schematically as follows:



Graphite is an allotropic form of a type of carbon where the atoms are located in hexagonal planes (graphens) separated by a distance of 3.32 Å. Carbon black consists of an aggregation of nanosize particles containing a crystalline part made of graphene lamellars and a noncrystalline part with functional groups [7,8]. Such nanoparticles aggregates are generally assembled in agglomerates which can reach sizes in the micrometer range. Acetylene black is a special type of carbon black obtained by cracking of acetylene at high temperature (up to 2400 °C), which shows specific properties, in particular enhanced electric conductivity because of its network-type morphology [9].

The most important of today's applications of carbon black is in the manufacturing of tires which accounts for about three quarter of its total consumption [6]. Carbon black is incoporated into a rubber-type material at a load up to 33 wt.% in order to improve its wear resistance, durability and mechanical properties [8–10]. Over the years, different types of elastomers have been used, often in blends, to produce tires showing the expected performance: natural rubber, polybutadiene, polystyrene/polybutadiene, polychloroprene, ethylene–propylene copolymer, polyurethanes. A number of studies have been devoted to the effect of the addition of carbon black in such elastomers [11–15], but the actual reasons of the observed improvement in performance are still not fully elucidated. Carbon black has also been used as filler in a variety of other polymers to produce composite materials showing improved mechanical and electric properties: epoxides [16] ethylene/butylacrylate [17], polyethylene [18], polyvinylidene fluoride [19], polypropylene [20], polystyrene [21], polymethylmethacrylate [22]. Conductive nanocomposites have been obtained by introducing graphite into various polymer matrices: polyaniline [23,24], polyarylene disulfide [25], polystyrene [26], polyamide [27]. A comprehensive survey of the numerous studies reported in the literature on carbon black and on carbon-based composite materials has been presented by Donnet et al. in a recent textbook [28].

All of these composite polymers have been obtained by a thermal processing. Ionizing radiation have been used to crosslink polyethylene/carbon composites [29], and electron beams for graphite/epoxide composite [30], as well as to induce the polymerization of carbon filled resins [31]. UV-radiations are commonly employed to rapidly dry printing inks, in particular black inks which consist typically of acrylic resins containing up to 15 wt.% carbon black [32]. Deep through cure can be easily achieved by UV-radiation in such opaque medium because the layer of ink deposited is very thin, typically 2 μm. Our objective was to use the same UV-curing technology to produce up to 40 μm thick coatings of carbon black nanocomposites by an adequate choice of photoinitiator, as well as of thicker samples by means of a dual-curable system.

2. Experimental

The photocurable composite resin was made of four major components: an acrylic monomer, an acrylate functionalized oligomer, a photoinitiator and the mineral filler. An acrylate end-capped polyurethane, PUA (Ebecryl 8402 from CYTEC) was used as telechelic oligomer (M = 1200 g). Hexanedioldiacrylate (HDDA) from UCB Chemicals was selected as reactive diluent at a weight concentration of 20% to reduce the formulation viscosity. A bisacylphosphine oxide (Irgacure 819 from Ciba Specialty Chemicals) was used as photoinitiator at a concentration of 1 wt.%. For the dual-curable resin, a redox initiator was added to the formulation: benzoyl peroxide (from Aldrich), in combination with dimethyl-*p*-toluidine (from Aldrich), at a weight concentration of 1% each.

Three types of carbon powder were selected as mineral filler to obtain a nanocomposite material: natural graphite (NG) from Prolabo, acetylene black (AB) from Showa Denko, and oxidized graphite (OG) by a treatment with potassium permanganate in acid medium (concentrated SO_4H_2). In order to obtain nanoparticles of carbon by destruction of aggregates and agglomerates, the resin was exposed to ultrasounds during 10 min (Branson Sonifer A450) at a frequency of 20 kHz and a power of 400 W, at 25 °C in the dark to prevent any premature polymerization.

The filled resin was hardened by a short exposure to UV-radiation which induces the crosslinking-polymerization of the acrylate double bonds. A medium pressure mercury lamp was used as radiation source: Minicure set up from IST operated at a belt speed between 5 and 50 m min^{-1} (exposure time between 1 and 0.1 s) and a fluence rate of 400 mW cm^{-2}. A radiometer (IL-390 from International Light) was employed to evaluate the UV-dose in the 280–400 nm wavelength range received by the irradiated sample. All the UV-curing experiments were performed at ambient temperature in the presence of air.

The nanocomposite samples were either UV-cured as 36 μm thick films or dual-cured as 2 mm thick plates, depending on the type of analysis performed (infrared spectroscopy or dynamic mechanical analysis, respectively), in relation to the different kinds of applications of such materials (coatings, moulds, cements, adhesives). To ensure that exfoliation of the graphene platelets has taken place in the liquid resin upon ultrasound treatment, the sedimentation of the carbon particles has been followed by visible spectroscopy (DU-7000 spectrophotometer from Beckman), monitoring the decrease of the absorbance at 550 nm as a function of time in a 1 cm thick cell.

The extent of the polymerization was evaluated by means of infrared spectroscopy (Bruker IFS-66 FTIR spectrophotometer), by monitoring the disappearance of the band at 812 cm^{-1} of the acrylate double bond after a given UV-exposure. The presence of carbon black (2 wt.%) does not affect the monitoring of this band, as it only causes a rise of the IR spectrum base line. The monomer conversion (x) was calculated from the relative decrease of the IR band absorbance: $x = (A_0 + A_t)/A_0$. No correction was made for shrinkage (~8%) because the thickness decrease is compensated by a concomitant increase of the functional group content. Exotherms of sample undergoing polymerization were measured by optical pyrometry (Testo 825-T2), the laser beam analyzing the 5 μm top layer of the sample.

The viscoelastic properties of 2 mm thick samples of dual-cured carbon black acrylate nanocomposites were determined by dynamic thermal mechanical analysis (DMA-Q 800 from TA-Instruments), by operating at a 1 Hz frequency and a 20 μm amplitude, with a 2 °C min^{-1} temperature rising rate. From the variation of the storage modulus (E') and of the tensile loss factor ($\tan\delta$) with temperature, values of the Young modulus and of the glass transition (or relaxation) temperature (T_g or T_α) were determined, respectively. Similar samples were used for evaluation of the resiliency or impact resistance (expressed in kJ m^{-2}) by means of a Mouton pendulum. The electric conductivity (C), expressed in Siemens (S) per centimeter of carbon black/acrylate nanocomposites was evaluated by measuring the resistance (R in ohm) of a 1 cm long sample cured between two metallic plates, and applying the equation: $R = C^{-1} l\ (\mathrm{cs})^{-1}$, where l is the sample length and cs its cross-section expressed in cm^2.

3. Results and discussion

3.1. Exfoliation of graphite

In a previous study on the synthesis of clay nanocomposite materials by light-induced crosslinking polymerization, we have shown that a simple way to ensure that exfoliation of the silicate platelets has taken place upon ultrasound treatment of the liquid resin and that a true nanocomposite has been formed upon UV-curing is by monitoring the sedimentation of the mineral particles. As expected, it was found to be much slower for nanosize particles than for microsize particles. The same method was used to evaluate the efficiency of the ultrasound treatment on the exfoliation of carbon black in an acrylic resin (hexanediol diacrylate). Fig. 1 shows the sedimentation profiles recorded by following the turbidity (absorbance at 550 nm) of the graphite (NG) filled liquid resin as a function of time, with and without ultrasound treatment. It can be seen that the turbidity remained essentially unchanged during 1 h for the sample sonicated during 10 min, while it was progressively clearing up for the untreated sample.

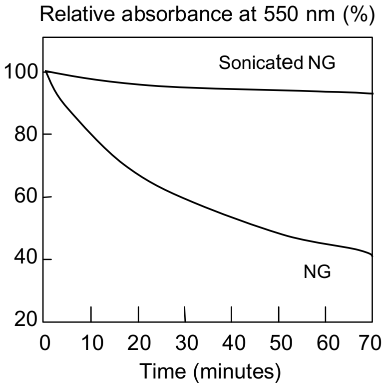


Fig. 1. Influence of the ultrasound treatment (10 min) on the sedimentation of natural graphite NG (0.1 wt.%) in hexanedioldiacrylate. Initial absorbance: 1.47.

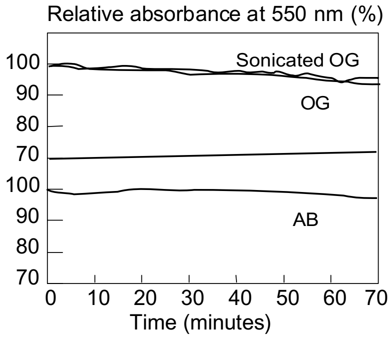


Fig. 2. Sedimentation profiles of oxidized graphite OG and acetylene black AB (0.1 wt.% each) in hexanedioldiacrylate. Initial absorbance: 1.5 and 2.0, respectively.

A different behavior was observed with both the oxidized graphite (OG) and the acetylene black (AB) where the sedimentation rate was much slower than for natural graphite (NG), as shown in Fig. 2. The ultrasound treatment was found here to have hardly any effect on the sedimentation rate. It can therefore be concluded that the size of the carbon particles in these two samples is much smaller than for natural graphite, probably in the nanometer range. While in the OG sample it is the oxidizing treatment which produces nanoparticles by destroying the graphite aggregate structure, in the AB sample it is the very mode of synthesis which generates nanosize carbon particles. It is quite remarkable that, after 10 h of sedimentation, the relative absorption at 550 nm was essentially the same (60% of the initial value) for the AB and OG samples as for the sonicated NG sample.

3.2. Synthesis of carbon nanocomposites by photopolymerization

The UV-curable polyurethane-acrylate resin used in this study was previously shown to polymerize rapidly upon UV-irradiation, with formation of a tight tridimensional polymer network [33]. Such photoinitiated crosslinking-polymerization, which is represented schematically in Chart 1, yields a hard and totally insoluble material within a fraction of a second. Fig. 3 shows the conversion versus time profile obtained by infrared spectroscopy analysis performed immediately after UV-exposure, for a 36 μm thick sample irradiated at ambient temperature in the presence of air. As much as 80% of the

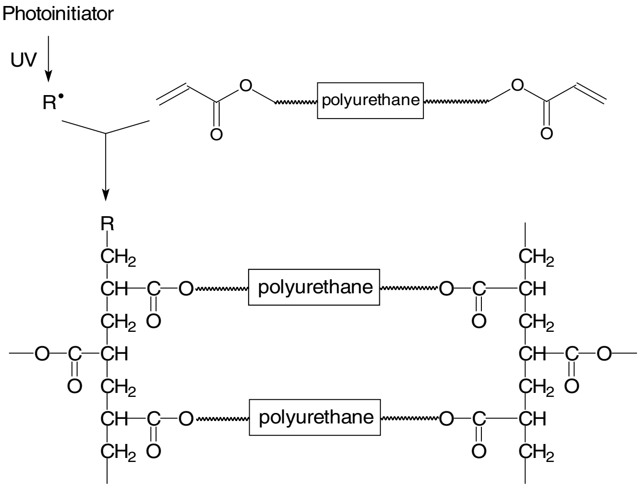


Chart 1. Photoinitiated cross-linking polymerization of a polyurethane-diacrylate.

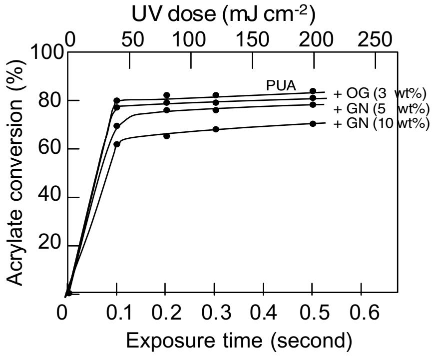


Fig. 3. Influence of the carbon filler on the photopolymerization of a polyurethane-acrylate (PUA) resin. Film thickness: 36 μm. Atmosphere: air. Light intensity: 400 mW cm^{-2}.

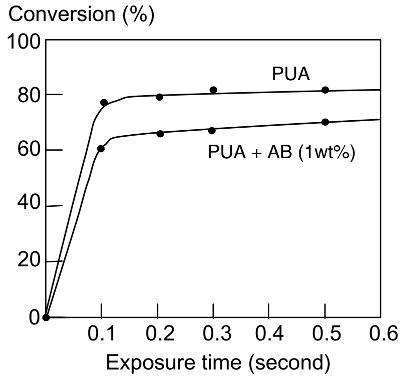


Fig. 4. Influence of acetylene black (1 wt.%) on the photopolymerization of a polyurethane-acrylate resin. Film thickness: 36 μm. Atmosphere: air. Light intensity: 400 mW cm^{-2}.

acrylate double bonds did polymerize within 0.1 s under such intense illumination, but the chain reaction did not proceed much further (up to a maximum 85% conversion) because of vitrification and related molecular mobility restrictions.

The addition of graphite (NG and OG) at a concentration of 3 wt.% was found to have no significant slowing down effect on the polymerization process, similar conversion versus time curves being obtained as with the unfilled resin, as shown in Fig. 3. The screen effect of the filler becomes more apparent at concentration superior to 5 wt.%, with a final conversion dropping from 85% to 75% when the graphite content was increased to 10 wt.%. In the case of acetylene black, this screen effect was found to appear already at a concentration of 1 wt.%, as shown in Fig. 4. The reason of this difference in behavior is that the opacity of the AB filled sample is much greater than the opacity of the samples containing NG or OG, probably because of a better dispersion of the carbon nanoparticles.

Consequently, to achieve a deep through-cure of thick samples it was necessary to associate a second curing process, by introducing in the acrylic resin a thermal initiator, like benzoyl peroxide. A few centimeter thick carbon black nanocomposite materials have thus been produced by heating at temperatures above 120 °C for up to 1 h. In order to reduce both the curing time and the temperature, we have selected a redox initiating systems consisting of benzoyl peroxide and a tertiary amine, dimethyl-*p*-toluidine. The production of free radicals results from electron and proton transfer between the two compounds according to the reaction scheme shown in Chart 2 [33,34].

Because of its short potlife, the formulation had to be used as a two-component system, one containing the peroxide and the other one the amine, at a concentration of 1 wt.% each [35]. Upon mixing of the two parts, the polymerization of the acrylate double bonds was found to proceed rapidly, already at ambient temperature. But the exothermicity of the reaction makes the temperature rise up to 90 °C within a few minutes for a 2 mm thick sample, as shown in Fig. 5 for the clear resin (curve a).

The addition of 1 wt.% natural graphite has no slowing down effect on the curing process (Fig. 5,

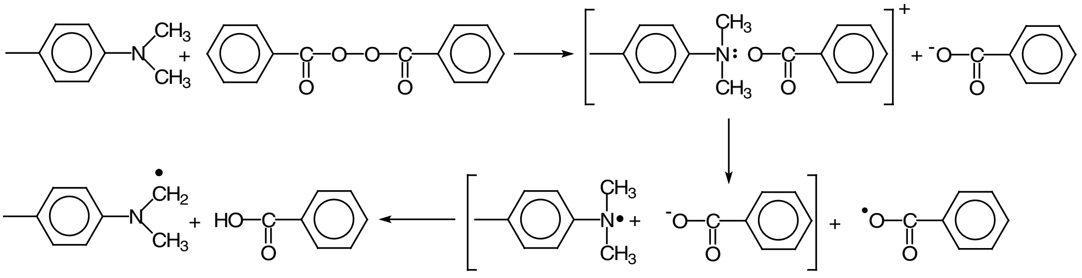


Chart 2. Decomposition of benzoyl peroxide in the presence of a tertiary amine.

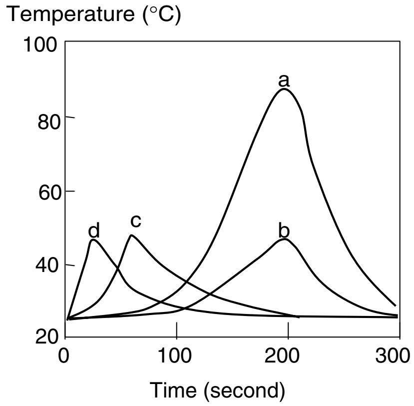


Fig. 5. Influence of the carbon filler on the temperature profile of a two-component redox-acrylic resin undergoing polymerization. (a) neat resin PUA, (b) PUA + 1 wt.% Natural graphite (sonicated), (c) PUA + 1 wt.% acetylene black; (d) PUA + 2 wt.% acetylene black. Support: PMMA; Film thickness: 2 mm.

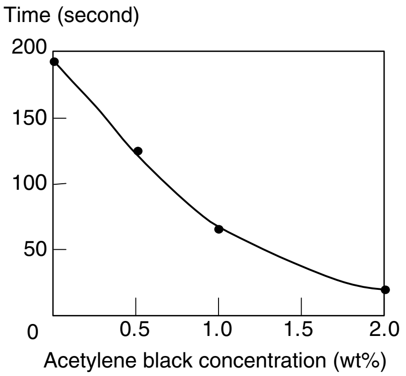


Fig. 6. Accelerating effect of acetylene black on the polymerization of a redox acrylic resin (PUA), as measured by the time to reach the maximum temperature.

Table 1
Influence of various factors on the maximum temperature reached upon redox polymerization of a clear acrylic resin

Support	Film thickness (mm)	Temperature (°C)	Reaction time (s)
PMMA	0.35	28	192
PMMA	0.70	32	200
PMMA	2.0	88	196
PVC	10.0	130	180
Copper (1 mm)	2.0	63	195
Steel (1 mm)	2.0	60	200
Steel (1 mm)	2.0	50	195

curve b), the maximum temperature being still reached after 200 s, but its value was significantly lower (47 °C) than for the clear resin. This is probably due to the well known effect of the carbon filler which can act as a heat trap. A quite different behavior was observed with the formulation containing acetylene black, where the polymerization was substantially accelerated (Fig. 5, curves c and d), the maximum temperature being reached within 20 s for the resin containing 2 wt.% AB. This catalytic effect of acetylene black, clearly illustrated by a plot of the reaction time versus the AB concentration (Fig. 6), is not well understood. It may be due to the formation of an activated complex between the acrylic resin and the carbon nanoparticles, which would accelerate the redox reaction and thus the production of initiating radicals. The presence of paramagnetic centers in carbon black has been detected by ESR spectroscopy. The unpaired electron was shown to be preferentially located at the surface of the carbon particles [36,37]. In the case of acetylene black, the presence of functional groups at the nanoparticles surface may also contribute for the enhanced production of free radicals.

It should be mentioned that the magnitude of the temperature rise in this redox polymerization depends not only on the formulation composition, but also on external factors such as the sample thickness and the type of support. As expected, the highest temperatures were reached for thick samples placed on insulating plastic supports, as shown in Table 1.

3.3. Properties of UV-cured carbon nanocomposites

The physico-chemical properties of photocrosslinked polymers depend primarily on the chemical structure of the functionalized oligomer, on the functionality of the monomer used as reactive diluent, as well as on the final cure extent [38]. They can be varied in a large range, depending on the considered application, from soft and flexible elastomers well suited for adhesives applications to hard and tough organic glasses well suited for protective coatings. The polyurethane-acrylate resin used in this study generates upon UV-exposure a polymer which belongs to the second class of material. Because of its high crosslink density (2 mol/kg), the UV-cured polymer exhibits excellent chemical and heat resistance. Total insolubilization was achieved within 1 s of UV-irradiation, with formation of a polymer which starts to decompose at temperatures above 350 °C.

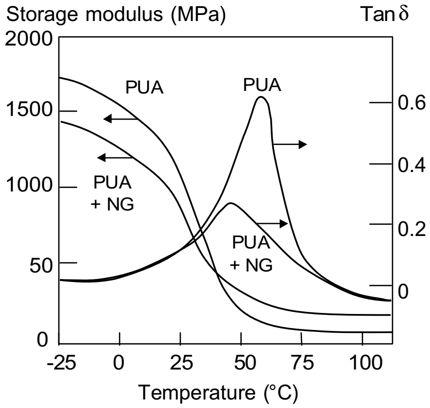


Fig. 7. Influence of natural graphite (5 wt.%) on the storage modulus (E') and the tensile loss factor ($\tan\delta$) profiles recorded by DMA for a redox-cured polyurethane-acrylate.

The addition of carbon nanoparticles was found to affect, to a certain extent, the viscoelastic properties by imparting to the nanocomposite polymer some flexibility and increased impact resistance. Fig. 7 shows some typical profiles recorded by dynamic mechanical analysis for a 2 mm thick redox cured samples, by monitoring the variation of the storage modulus (E') and of the tensile loss factor ($\tan\delta$) with increasing temperature. It can be seen that the addition of the carbon nanoparticles (5 wt.% of natural graphite, and sonication) causes a small decrease of the glass transition temperature (from 57 to 45 °C) and of the Young modulus (from 1050 to 820 MPa). A similar flexibilisation effect was observed by addition of the oxidized graphite particles, as shown by the data reported in Table 2. As a result of the decreased rigidity, the UV-cured nanocomposite material becomes more resistant to shocks. The resiliency, measured by a Mouton pendulum on 2 mm thick samples, was found to increase from 34 kJ m^{-2} for the neat polymer up to 57 kJ m^{-2} for the carbon nanocomposite. A similar but less pronounced effect was observed by introducing small amounts of acetylene black (1 wt.%) into a more flexible polyurethane-acrylate matrix (Table 2).

Table 2
Influence of carbon nanoparticles on the properties of a polyurethane-acrylate (PUA) polymer

Cured resin	T_g (°C)	Young modulus (MPa)	Resiliency (kJ m^{-2})
PUA-1	57	1050	34
PUA-1 + NG (5 wt.%)	44	820	55
PUA-1 + OG (5 wt.%)	43	720	57
PUA-2	48	830	17
PUA-2 + AB (1 wt.%)	42	410	23

It should be mentioned that the addition of carbon nanoparticles causes a drastic loss of the gloss of such acrylic polymers, as observed previously with clay and silica nanoparticles [5]. This matting effect was shown to result from the increased surface roughness, which makes also the surface of the nanocomposites material less slippery, as requested for some floor finishes applications. These polyurethane-acrylate/carbon nanocomposites show an excellent resistance to photodegradation, because of their high crosslink density and of the presence of the carbon filler which acts both as a radical scavenger and a UV-screen. They are therefore well suited for coatings applications to improve the weathering resistance of organic materials (wood, plastics, fabrics, paper) used in outdoor applications, if a black appearance is accepted.

With respect to the electrical conductivity of such carbon nanocomposites, a significant effect could be detected only at very high loads of graphite (NG and OG), above 30 wt.%. A quite different behavior was found by using as filler acetylene black, where some electrical conductivity could already be measured at concentrations above 1 wt.%, as shown in Fig. 8. The electrical conductivity was found to rise exponentially with increasing concentration of acetylene black to reach a value of 35 mS/cm at a load of 2.5 wt.%, and 600 mS/cm at 10 wt.%. This effect could be attributed to the network structure and string-like morphology of acetylene black together with the large specific area of the nanosize AB particles. The electrical conductivity of carbon black

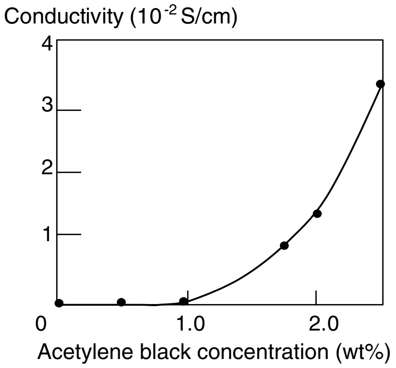


Fig. 8. Influence of the acetylene black content on the electrical conductivity of a redox-cured PUA nanocomposite.

was shown to increase with decreasing particle size and average particle distance [39,40]. To obtain highly conductive carbon-based nanocomposite materials, acetylene black appears to be the choice candidate. By using the two-component redox acrylic resin as a glue, we have succeeded in assembling within minutes two metallic plates, without a substantial loss of electrical conductivity. Such a conductive glue is particularly easy to use, by applying a thin layer of one component on one part of the assembly and the second component on the other part, and by pressing the two parts together to a strong bonding was achieved within 1 min, at ambient temperature.

4. Conclusion

Polymer nanocomposites have attracted growing attention in the past few years, owing to their unique characteristics, and they have found a number of applications in various industrial sectors (automotive, electronics, aeronautics). We have developed a simple method to synthesize rapidly at ambient temperature carbon-based nanocomposite materials by photo- or redox-initiated polymerization of a solvent-free acrylic resin. The very low emission of volatile organic compounds, together with the minor energy consumption, makes this curing technology particularly attractive in consideration of today's growing concern in the chemical industry for environment-related issues. The presence of carbon nanoparticles was found to lower the glass transition temperature of the polymer and make it more flexible and impact resistant. These highly crosslinked nanocomposite polymers are quite resistant to organic solvents, heat and weathering, as well as to mechanical aggression. They are therefore well-suited for coatings applications to protect and improve the surface properties of different types of materials. The two-component redox based resin containing acetylene black can also be used as a glue to assemble metallic parts or wires, without much loss of electrical conductivity.

This UV-radiation and redox curing technology is not restricted to the synthesis of carbon/acrylate nanocomposites, but it can be extended to other types of polymer systems, such as crosslinked thiol/polyenes, unsaturated polyesters and interpenetrating polymer networks, as well as to other types of layered nanoparticles. Further work should be oriented in such directions to take full advantage of the remarkable performance of this environment-friendly and cost-effective method of producing nanocomposites polymers.

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