MWCNTs FOR TUNING VISCOELASTIC AND INELASTIC PROPERTIES OF ELASTOMERIC MATERIALS

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Abstract
Nanocomposites based on thermoplastic polyurethane (TPU) reinforced with multiwalled carbon nanotubes (MWCNTs) have been prepared with different concentrations (0.1, 5.0 and 20.0% by volume). The effects of MWCNTs addition into TPU upon viscoelastic and dissipative properties have been investigated at both small and high strains. Dynamic mechanical tests performed at small strains have shown that either storage modulus or loss tangent of the reinforced TPU increase with nanotube content. Cyclic tensile tests have illustrated that at high strains (100-300%) the fraction of dissipated strain energy increases with the amount of MWCNTs (even of one order of magnitude). SEM investigation and SAXS measurements of strained and unstrained TPU samples have provided indications about the dissipative phenomena in the nanocomposite systems. Nanocomposite TPU films were inserted within rigid glassy thermoplastic plates in order to produce a model composite system with an interleaved damping layer. The investigation of dynamic mechanical properties of such system has shown that nanotubes addition into damping layer restrains the flexural properties reduction and, at same time, increases impact (100-167%) and damping properties (69-149%).

1 Introduction
The addition of carbon nanotubes into polymeric matrix can result in an increase in both elastic and dissipative properties [1-6]. Nanotubes reinforcement effect is due to their very high elastic modulus (~ 1 TPa) while damping properties (dissipative properties) arise from the mismatch between elastic moduli of reinforcement and hosting matrix, that in turn causes the nanotube/matrix interface sliding as strain increases [1-6]. These mechanisms have been widely investigated in reinforced systems based on rigid polymers but mainly limiting the analysis to low strains.
In the current work a thermoplastic polyurethane (TPU) reinforced with multiwalled carbon nanotubes (MWCNTs) has been produced and tested with a focus on the high deformability of this system that allowed to gain insights on dissipative mechanisms even at high strains (up to 300%) by exploring the inelastic behavior. Thermoplastic polyurethane (TPU) is a block copolymer made up by alternating soft and rigid segments. The hard segments are formed by addition of a chain extender, such as butadiene diol, to the isocyanate (methylene-diphenyl

diisocyanate). The soft segments consist of flexible polyether or polyester chains (polyols) connecting two hard segments. The soft and hard segments are incompatible at room temperature and aggregate into soft (SDs) and hard domains (HDs), respectively, resulting in a polymeric system schematically represented as HDs formed amid the rubbery SDs. The hard segments have a much higher melting point and polarity than much less polar and low-melting soft segments. Morphology significantly affects final properties of the TPU. In fact, the size, crystallinity and interconnectivity of the HDs, as well as the nature of domain interface and the mixing of hard segments in the soft segment phase, influence most of physical properties such as elasticity and toughness. SDs form an elastomeric matrix responsible for the elastic properties of TPUs, while HDs act as both cross-links and reinforcing fillers [7, 8]. Consequently, nanotubes addition into TPU affects microdomain morphology characteristics, such as HDs interdomain spacing that can be detected by small angle x-ray scattering (SAXS) [7, 8], and determines viscoelastic and inelastic properties of the TPU system. In the current study morphology variation has been correlated to two different types of nanotubes at several concentrations.
The developed TPU systems have been used to prepare thin films to be interleaved in rigid polymeric plates in order to study the effect of nanotube content (in the elastomeric matrix) on both viscoelastic and inelastic properties of the interleaved configuration systems.

2 Materials and testing methods

Thermoplastic polyurethane (TPU) Desmopan DP 9370AU supplied by Bayer (Germany), has been used as elastomeric matrix. Two types of multiwalled carbon nanotubes have been dispersed in the matrix: NANOCYL^{TM} NC3150 (average length< 1.0 μm, average diameter =9.5 nm) purchased by Nanocyl (Sambreville, Belgium) and MWCNTs 636509-2g (outer diameter 10-30 nm, inner diameter 5-10 nm, length 0,5-500 μm) purchased by SigaAldrich. In the following nanotube purchased by Nanocyl and SigmaAlrdich will be indicated MWCNTs_NC and MWCNTs_SA, respectively. MWCNTs were ultrasonicated by a dipping tip sonicator (Misonix S3000, NY-USA) for 60 min at room temperature in THF (0.1 % volumetric solution of nanotube) by providing 18 watt power. In the ultrasonicated solution TPU pellets were successively added and mixed with magnetic a stirrer for 6 hrs. The solution was then poured in a Petri dish in order to allow THF evaporation (at room temperature for 12 hrs) and obtain reinforced TPU films. Such films were further dried in a vacuum oven at 90° C for 24 hrs. The dried films were cut and overlapped to prepare thicker flat samples (0.5 mm thick) by hot pressing (through heated plates hydraulic press, model P 300P, Collin Gmbh, Germany). TPU samples reinforced with 0.1, 5.0, 20.0 % by volume of MWCNT_SA and with 0.1, 5.0 % by volume of MWCNT_NC were prepared. From the TPU thin sheets, specimens 50 mm long, 8 mm wide and 0.5 mm thick were cut. Tensile test with a Tensile mechanical tests were performed on TPU specimens by using an Instron 3310 universal testing machine (Norwood, MA, USA) with a cross-head speed of 50 mm/min at room temperature. Load-unload cycles carried out on TPU specimen at the same rate of tensile tests with progressively higher nominal strains (0.05, 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0) without dwell time when the deformation direction changed. By integrating the load-unload stress-strain curves the specific work input and dissipated strain energy was obtained [1, 2]; in particular integration in load segment of the curve gives the specific work input in correspondence of fixed strain (equivalent to total strain energy), while the integration including the unload section of the curves provides the dissipated strain energy (inelastic fraction of strain).
Viscoelastic properties of TPU samples (2.0 mm long, 5mm wide and 0.5 mm thick) were investigated in tensile deformation with a Dynamic Mechanical Analyzer DMA Tritec 2000 (Triton, UK) at 30° and 1 Hz.

Scanning electron microscopy (SEM) analyses were performed on polymeric samples by analyzing their surfaces with a Quanta 200 FEG from FEI (Eindhoven, The Nederlands). All samples were coated with gold before analyses in order to make conductive their surfaces.
The TPU films reinforced with MWCNTs_SA were inserted within rigid thermoplastic plates and, through hot pressing at TPU softening temperature (170°C), consolidated composite systems with an interleaved damping layer were produced. Viscoealstic properties of such systems were investigated by means of DMA Tritec in dual cantilever deformation and strain sweep mode at 30 °C and 1 Hz.
Impact properties of interleaved system were measured with a Drop Weight Impact Test System Fractovis CEAST 9350 (Instron-CEAST, Italy) equipped with instrumented impact dart.

3 Results and Discussion

Dynamic mechanical tests have shown that nanotubes addition into TPU matrix results in increased storage modulus and loss tangent (Fig. 1). As the amount of MWCNTs increase linear region reduces evidencing a dynamic behavior dominated by the Payne effect [9]. The reinforcement of MWCNT_NC is more effective with respect that of MWCNT_SA type as the storage modulus of TPU+5.0% MWCNT_NC is higher than TPU+20.0% MWCNT_SA modulus. Samples containing 0.1% of carbon nanotubes presented a slight modulus decrease probably related to the interaction with hard domains that leads to a matrix modulus reduction (loose of continuity of HDs network) not counterbalanced by nanotube reinforcement at this low filler loading. A similar trend has been detected also by tensile tests (Fig. 2); TPU+5.0% MWCNT_NC presented a substantial enhancement of strain specific work input which was considerably higher than the equivalent TPU sample reinforced with 5.0 of MWCNT_SA. Such a difference can be ascribed to physical properties (diameter, length, out-of-axis mechanical properties, surface properties, etc.) of these two types of nanotubes that result in either different dispersions into hosting matrix or different micro-domain morphology, as shown in the following.

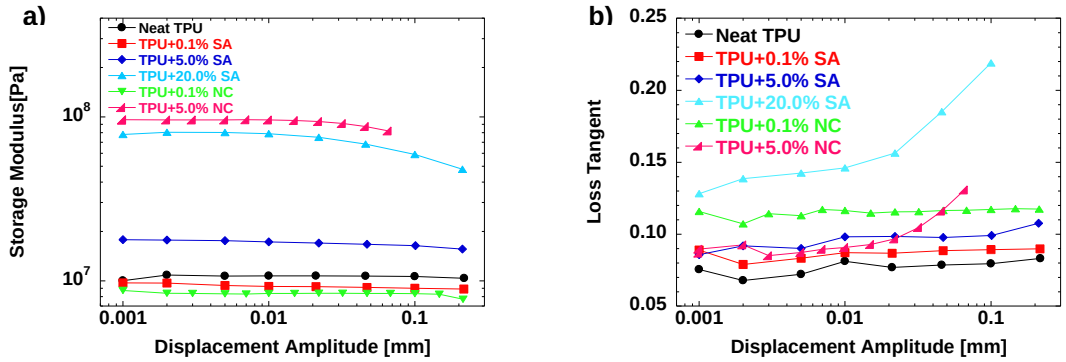


Figure 1. Storage modulus (a) and loss tangent of TPU film sample measured with strain sweep test performed at 30°C and 1 Hz.

In order to investigate the inelastic properties at high strain, tensile cyclic tests were performed on TPU systems; in Fig. 3a a cyclic test of TPU+5.0% MWCNT_NC is reported and compared with a not cyclic tensile test: the loading portion of cyclic tests (apart from cycles themselves) overlap with standard (non cyclic) test indicating that in the investigate strain range the sample is not affected by plastic deformation induced by load-unload cycles at higher progressive strains (Fig. 3a). This behaviour permits to assume that dissipated strain energy calculated as the un-recovered energy in cyclic experiment is a fraction of the specific

work input measured in plain (non cyclic) tensile tests. The dissipated strain energy in neat TPU and TPU+0.1% MWCNT_NC samples is almost similar and a slight increase in the reinforced sample is detected at higher strains (Fig. 3b). The sample reinforced with 5.0% of MWCNT_NC presents a substantial increase of dissipated strain energy with respect to that of neat sample. TPU samples reinforced with MWCNTs_SA presented a trend similar to specimen containing MWCNTs_NC but with a lower increment.

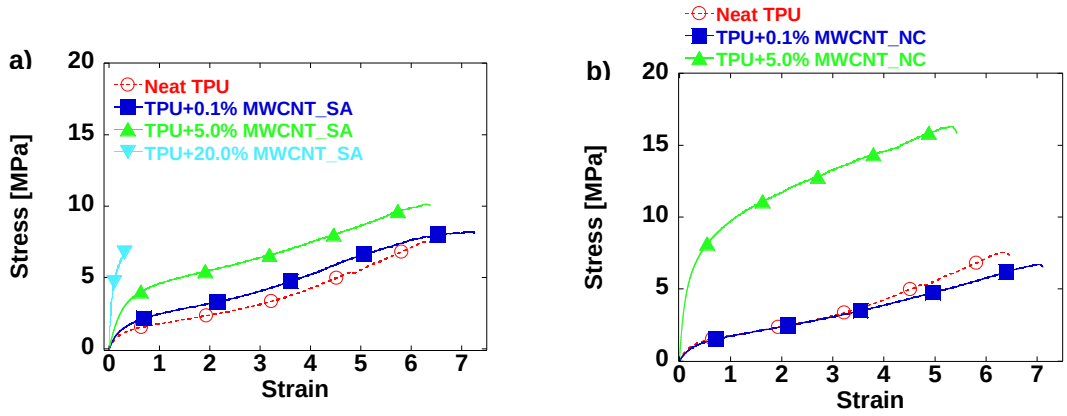


Figure 2. Tensile test of TPU film reinforced with MWCNTs_SA (a) and MWCNTs_NC (b).

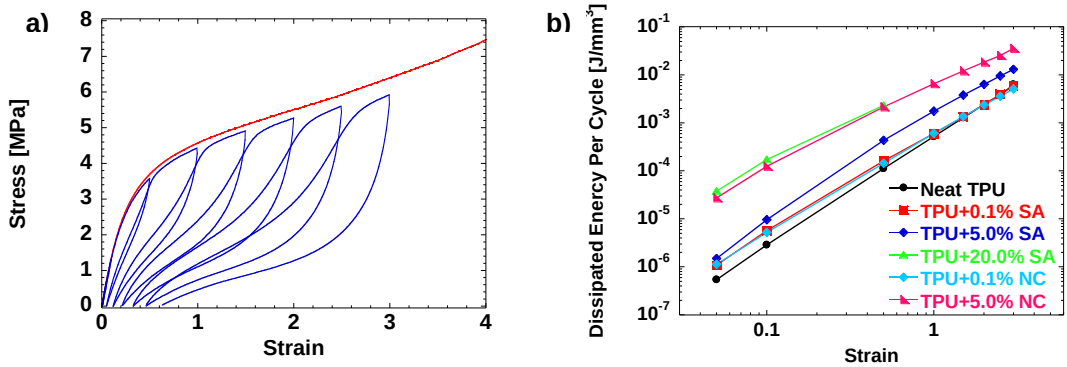


Figure 3. Comparison of tensile test and tensile cyclic test of TPU+5.0% MWCNT_NC sample (a) and dissipated strain energy per cycle as function of tensile strain of TPU samples.

From the analyzed results so far, it is possible to infer that the nanotubes physical properties dictate the viscoelastic and inelastic features of TPU. SAXS scattering profiles have shown that nanotubes modify TPU microdomain morphology and their state of aggregation at nanoscale varies with their type (Fig. 4). In details, the broad scattering feature observed in the region 0.3-0.8 nm^{-1} may be associated to the interdomain distance between neighbouring hard domains [10], whereas the intensity at low q values (i.e q lower than 0.3nm^{-1}) is ascribed to the scattering of MWCNTs objects as individual tubes or small ropes [11]. The higher the filler content, the higher the scattered intensity at low q values. However composite filled with MWNTs_SA show a higher increase of intensity scattering compared to MWNTs_NC, pointing out that coarser nanotube aggregates are formed. Contrary to the MWNTs_SA, the MWNTs_NC exhibit a peculiar feature at q value equal to 1.0 nm^{-1} (see spectrum of TPU+5%NC) which may be reasonably attributed to the cross-section of CNT when they pack side by side in ropes structures [12]. This confirms that MWNTs_NC and MWNTs_SA

exhibit different morphology. The MWCNTs-NC are better dispersed at submicron length scale whereas they present ropes or bundles at nano length scale.
The separation distance between TPU hard domains, L is determined from the Lorentz corrected plot (see Figure 4b)), by using Bragg's equation [13]:

$$L = \frac{2\pi}{q_{\max}}$$

where $q_{max}$is the scattering vector corresponding to the maximum $I(q)q^2$ value. The separation distance increases with carbon nanotubes as confirmed by the q_{max} moving from 0.7nm^{-1} of neat TPU to lower values of composite materials. In particular the materials with MWCNTs_NC exhibit separation distance values slightly higher than the samples filled with MWCNTs_SA. This may be tentatively ascribed to the presence of ropes which induce a larger separation upon the segregation of hard domains.

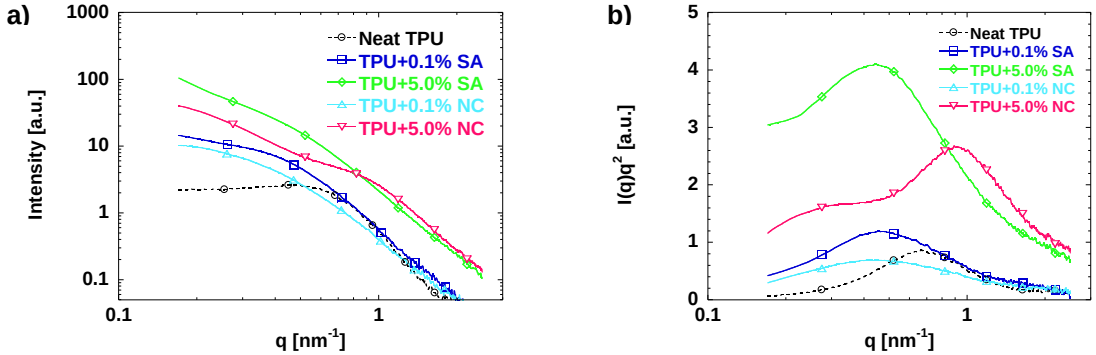


Figure 4. Scattering profiles (a) and Lorentz corrected plot (b) of TPU samples.

The surface of TPU samples reinforced with MWCNTs analyzed by electronic microscopy after straining has shown that nanotubes slide within the matrix because of the limited interfacial shear strength. This mechanism contributes to increase strain energy dissipation also in rigid polymers, as mentioned, but for high deformability matrices it is predominant taking into account either the higher achievable strain values.
In general, the dissipative mechanisms in such elastomeric systems can be identified by three main classes: 1) mechanisms related to viscoleastic and inelastic properties of the matrix, 2) inelastic mechanism of nanotube (plastic deformation, rupture and viscoelastic properties), 3) mechanisms governed by matrix/nanotube interface properties. The increase in loss tangent at low strains and the Payne effect (Fig. 1) are determined by variation of physical properties (entanglement density, etc.) in the matrix surrounding nanotubes [7], indeed mainly related to the first mechanism. While at high strains the other two mechanisms, and mainly those dominated by interface properties, contribute in very large amount to strain energy dissipation because the effect of matrix gradient properties around nanotubes become negligible at high strains. It is worth to point out that in case of weak nanotube/matrix interfacial shear strength, such as in the studied systems in which nanotubes have not surface functionalization, the strain energy dissipation due to inelastic properties of nanotubes themselves is limited by the huge mismatch between mechanical properties of matrix and reinforcement that prevent nanotubes to reach high deformation and failure.

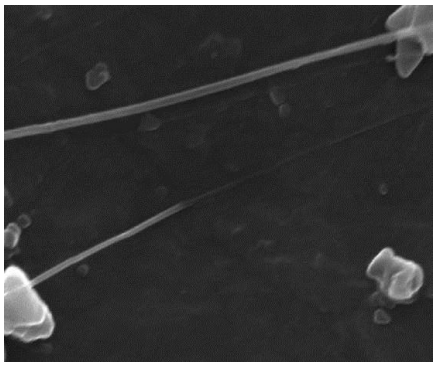
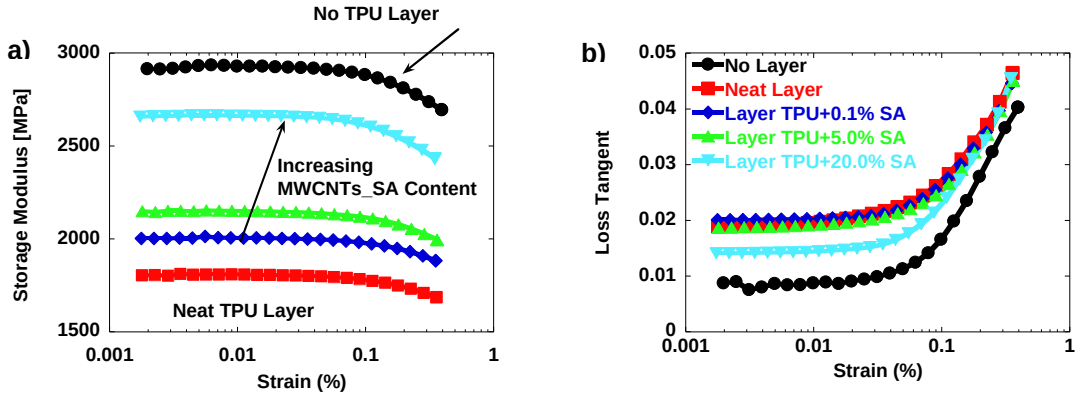


Figure 5. SEM image of TPU+5.0% MWCNTs_SA surface after straining at 300% (image size: 6.0x5.0 μm^2).

TPU films reinforced with MWCNTs_SA have been used to produce interleaved configurations in order to explore the effect of nanotubes in the elastomeric layer on damping and impact properties of this "model" composite system (Fig. 6).

Figure 6. Interleaved configuration with outer layers made out of styrene-acrylonitrile (SAN, Young's modulus 3.0 GPa) and reinforced TPU as damping layer (t_1=1.0mm, t_2=60 μm).

The storage modulus of the sample with neat interleave drops with respect to undamped system but the addition of nanotubes increments the storage modulus monotonically with MWCNTs_SA content (Fig. 7a) towards values of the undamped configuration. The loss tangent of interleaved configuration stepped up more than 100%, in the investigated concentration, except for the composite interleaved with TPU+20%MWCNTs_SA that presented an enhancement of 69% (Fig. 7b and 7c).



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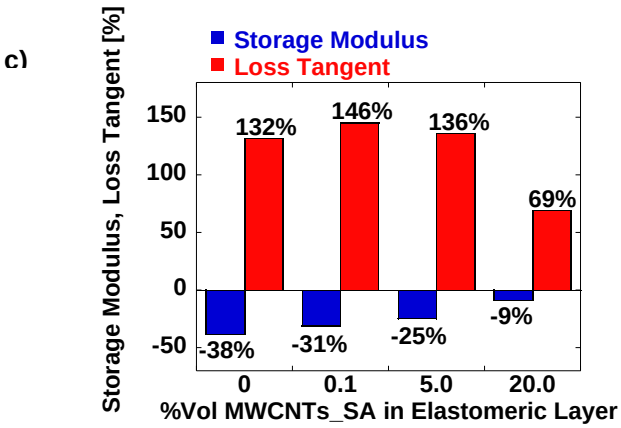

Figure 7. Storage modulus (a) and loss tangent (b) of interleaved configurations with TPU based damping layer reinforced by MWCNT_SA, measured in dual cantilever mode at 30°C and 1 Hz. (c) Increment of the loss tangent and the storage modulus of interleaved configurations with respect undamped system as function of nanotube content.

The improvement of storage modulus is determined by the stiffening effect of nanotubes in damping layers and the gain in loss tangent is due to the increase in loss tangent of TPU matrix as consequence of nanotubes addition; this latter effect is evidently related to viscoelastic properties of reinforced TPU at low strain (Fig. 1) and to dissipative mechanisms of the hosting matrix itself.

Impact tests on interleaved systems highlighted benefits due to the incremented dissipative energy fraction at high strain in reinforced TPU; in fact, the absorbed energy after the impact increased of 100% by interleaving neat TPU as damping layer and the addition of 5.0% by volume of nanotubes resulted in a further 66% improvement with respect undamped system (Fig. 8).

The possibility to control viscoelastic properties at low strains and strain energy dissipation at high strain of elastomeric TPU with MWCNTs concentration and type can be exploited as design tool of materials for high performance applications. In addition, the investigated elastomeric system presented unique properties with respect to viscoleastic properties since the stiffening of nanocomposite matrix results in a decrease of damping (loss tangent) for most of matrices [14, 15].

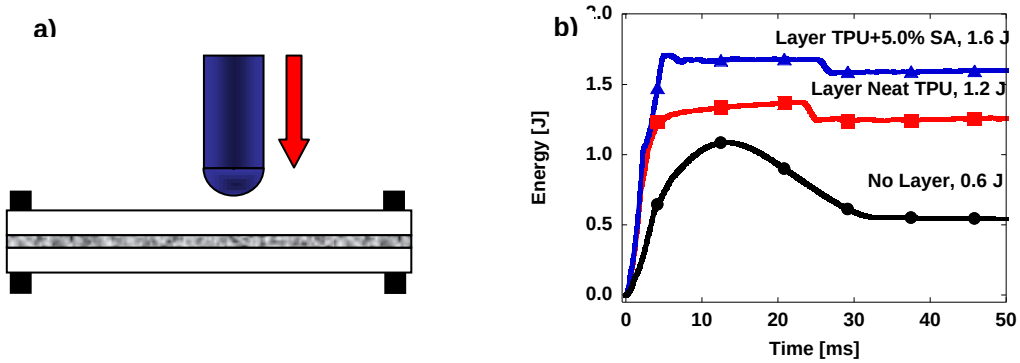

Figure 8. Impact configuration (a) and energy measured during the impact of not interleaved system, interleaved system with neat TPU and TPU+5.0% MWCNTs_SA damping layers.

Conlusions

MWCNTs are able to reinforce elastomeric TPU and at same time to increase its damping properties. Such features are dependent on physical properties and content of nanotubes indeed can be tuned for specific applications such as damping layers in interleaved

configuration. The studied model of interleaved configuration has shown to exploit the improvements triggered by nanotubes: increase in loss tangent higher than 100% keeping down modulus reduction, increase in energy absorption during impact test higher than 166% .

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