

Poly(propylene) Composite with Hybrid Nanofiller: Dynamic Properties

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ABSTRACT: Mechanical, impact, and relaxation properties of *in situ* synthesized carbon nanotubes-polyaniline (CNT-PANi) hybrid nanoparticle-filled poly(propylene) (PP) composites with or without an amphiphilic dispersing agent were investigated using tensile testing, notched Charpy impact testing, and dynamical mechanical testing methods. The reference material was MWCNT filled PP composite. Ethyl gallate (EG) was the dispersing agent which realizes high conductivity in PP composites with hybrid filler. Measured properties showed quite similar behavior of CNT-PANi hybrid and neat CNT filled composites. Addition of 20% EG in PP did not cause essential differences compared to the neat PP. When the dispersing agent was added in filler containing PP composites, remarkable effects were observed, especially in PP-hybrid composites. Mechanically, these materials had improved tensile properties, but they were brittle compared to the materials without dispersing agent. Dynamic mechanical analysis showed improvement in storage modulus, and in loss modulus the α transition was well observable. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 3734–3742, 2013

KEYWORDS: conducting polymers; mechanical properties; nanocomposites; poly(propylene); relaxation

Received 7 January 2011; accepted 10 August 2012; published online 10 October 2012

DOI: 10.1002/app.38532

INTRODUCTION

Nanocomposites are one of the most attractive materials to realize new properties in polymeric materials. Carbon nanotubes (CNT) based composites are today a subject of intensive research and development. Mechanical and electrical properties in composites are typical subjects which can be promoted by CNT. During the three last decades, inherently conductive polymers (ICP) have been used to produce high conductive polymeric materials and composites. To create conductive composites using hybrid filler systems consisting ICP and CNT is an alternative route, which may lead to new application. The successful material design requires balancing of a wide range of properties, and mechanical properties are a typical stumbling stone of conductive composites.

Strength properties of individual CNT are considerable, strength values from 11 up to 63 GPa, modulus about 1 TPa, and 12% strain are reported.¹ Reinforcing effects of CNT in composites are remarkable, but there are several matters those have effects on reinforcing characteristics, such as dispersion and interfacial bonding, especially in melt-blended composites.² Typical amount of CNT in PP composites is below 5%.^{3–5} A widely used approach is to modify surface of CNT. Polyaniline (PANi) has been polymerized on the surface of nanotubes to control conductivity properties.^{6,7} An undesired phenomenon caused by higher CNT loadings (>1–2%) is decreasing of some mechanical properties, especially observed in impact strength.⁸

Transitions are a key issue for mechanical properties of polymeric materials. The local dynamics of chains in isotactic polypropylene (iPP) includes three main relaxations, usually labeled as α , β and γ in order of decreasing temperature. γ relaxation is observed at about -60°C , and the origin is local motions in the amorphous phase.⁹ β relaxation corresponding to the glass transition is observed approximately at 0°C and is cooperative motions of chains in amorphous phase.^{10,11} α Relaxation, measured usually at temperatures between 50 and 100°C , is arising from local motions in the crystalline phase.¹²

In semicrystalline polymers, such as in iPP, crystallinity has a strong impact on these relaxations, not only on α transition, but also on β and on γ relaxations.¹³ Fillers and other additives which can control crystallization may have strong vicarious impact on the α relaxation.^{14–16} Nanofillers can affect relaxations by controlling crystallization at melt and/or by particle-polymer chain interactions at solid state. High crystallinity may mask nanofiller-based phenomena.¹⁷

Effects of nanofiller on T_g are not unambiguous. Increasing transition temperature is attributed on hindering of polymer chain mobility caused by interactions between nanoparticles and polymer chains.¹⁸ The opposite effect is explained by non-equilibrium state with excess free surface of voids.¹⁹ In some cases, the glass transition has disappeared or polymer matrix has been nonsensitive on nanofillers.^{20,21} The model presented by Lee et al.²² describes this phenomenon by a specific

Table I. Mechanical Properties

Materials	Tensile strength			Elongation		Charpy impact strength	
	MPa	s.d.	E-mod (MPa)	At max load (%)	At break, (%)	kJ/m ²	s.d.
PP	21.7	0.5	1110	6.7	>300	12.2	1.5
PP + 1% hybrid	25.4	2.9	971	6.8	195	14.1	2.2
PP + 3% hybrid	21.9	0.9	1230	6.4	>300	14.0	0.5
PP + 5% hybrid	22.4	1.6	1009	7.1	156	16.7	1.1
PP + 7% hybrid	23.4	0.1	1470	6.6	73		
PP + 10% hybrid	24.1	0.4	1370	7.6	46	23.5	5.1
PP + 12% hybrid	24.6	0.7	1440	8.2	36		
PP + 5% CNT						31.7	7.7
PP + 10% CNT	24.9	0.9	1480	8.7	42		
PP + 20% EG	21.3	0.3	1370	6.6	219	12.4	1.8
PP(20%EG) + 10% hybrid	24.2	0.4	1800	3.9	9.8	3.9	0.4
PP(20%EG) + 5% CNT						3.8	0.4
PP(20%EG) + 10% CNT	24.7	0.6	1920	4.1	9.3		

interaction between polymer and nanoparticles. Less attention is focused on the low temperature γ transition in PP although it has an essential role in impact properties at low temperatures.

Organic–inorganic hybrid nanomaterials are a new existing group of materials, where the combinations of organic and inorganic materials give a freedom to tune properties of these materials. In our previous work, we studied PP composites with *in situ* synthesized CNT-PANi hybrid fillers where nanotubes were coated by a thin inherently conductive polymer layer.²³ Amphiphilic dispersing agents promote conductivity of these composites and values up to 26 S/cm was measured using ethyl gallate (EG) as a dispersing agent. The molecular recognition phenomenon between PANi and EG has been predicted by Ikkala et al.,^{24,25} which was the motivation to use EG.

Electrical properties of conductive composites are the key issue in many products, although good mechanical properties of these materials are a precondition for realistic applications. The goal of this work was to analyze mechanical properties of PP composite with *in situ* synthesized CNT-PANi hybrid filler and effects of the amphiphilic dispersing agent on these composites.

EXPERIMENTAL

Materials

Polypropylene Domolen 2600 *M*, a heterophasic copolymer with MFI 7.5, was used as a matrix polymer. According to data-sheet, this PP grade combines a good stiffness with an excellent impact strength.²⁶ EG, C₆H₂(OH)₃COOC₂H₅, was obtained from Fluka (Cat. No. 48640). Multiwalled CNTs with purity >87%, Nanocyl NC7000 (average diameter 9.5 nm and average length 1.5 μ m, surface area 250–300 m²/g), were purchased from NanoCyl S.A. CNT-PANi hybrid material with CNT : PANi ratio 1 : 0.3 was produced by *in situ* synthesis polymerizing aniline in the presence of CNT (Nanocyl NC7000) and using phenolic sulphonic acid as a dopant ion. The PANi salt is attached on the CNT surface for a thin conductive PANi layer

covering some parts of the CNT surface and so forming a CNT-PANi hybrid material. The hybrid product was washed several times with water and dried using freeze dryer. The water content of the hybrid was 2.6% after drying. Detailed information about the PANi synthesis on CNT surface to form hybrid material is presented in the previous article from authors.²³ For the hybrid material, TGA analysis was carried out.

Compounding and Moulding

Before compounding, PP and fillers were dried in oven in 60°C over night. Compounds were produced using a miniature, corotating twin screw extruder (Thermo Haake Micro Compounder) at a temperature of 200°C for 1 min at a screw rotation speed of 100 rpm and in material batches of 6 g. Compounds were discharged in a miniature moulding machine (Thermo Haake Mini-Jet) and moulded at 220°C into samples with a mould temperature of 40°C, injection pressure 350 bars for 3 s, and post pressure of 160 bars for 5 s. After injection moulding, all samples were stored in a standard atmosphere room (23°C, humidity 50%) for 1 week before testing procedure.

Tensile Testing

Tensile testing was performed according to SFS-EN ISO 3167:2003 using Instron 4505 mechanical test equipment. Samples were dog bone-shaped standard samples, and results are an average of five parallel samples.

Impact Testing

Charpy impact test was made according to ISO 179 using Resil 5.5 (CEAST) impact test equipment with notched samples and 2 J hammer and 80 \times 10 \times 4 mm³ samples bars. Results are an average a five parallel samples.

DMTA

Dynamic mechanical thermal analysis was performed by Metler Toledo DMA/SDTA861e equipment in the tensile mode with dynamic deformation of 10 μ m at 1 Hz frequency. The heating

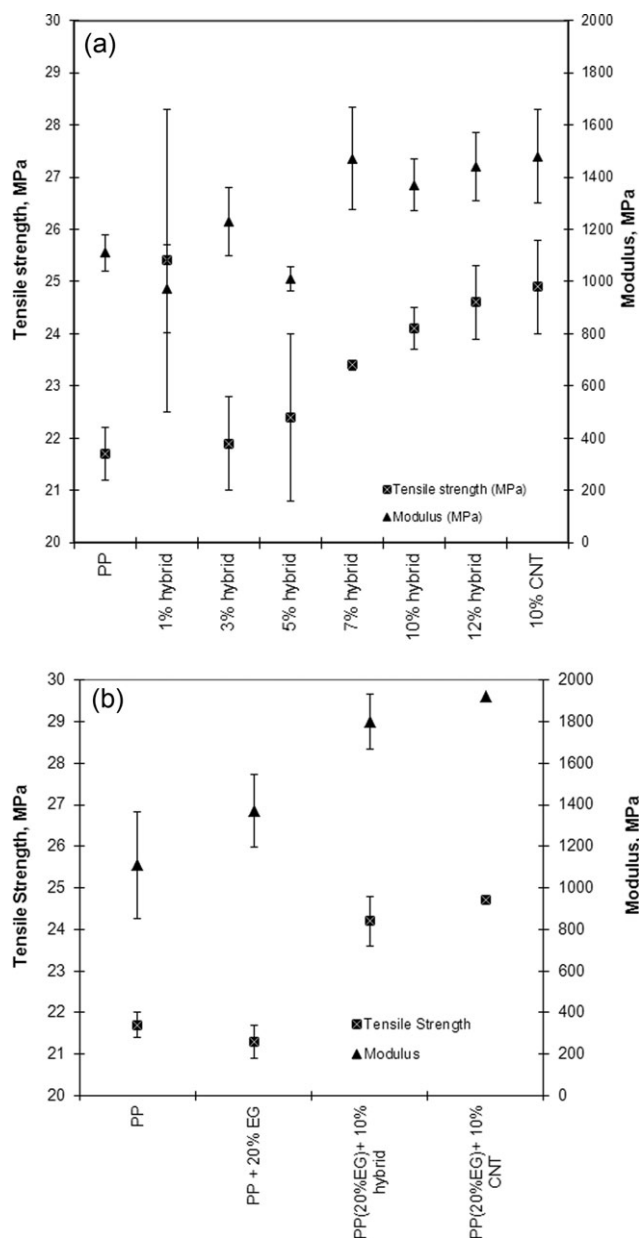


Figure 1. Tensile strength and modulus for PP with hybrid fillers or CNT without EG (a) and with EG (b).

rate was 3°C K/min. Samples were bars with dimensions $9 \times 3.5 \times 1 \text{ mm}^3$.

RESULTS AND DISCUSSION

Mechanical Properties

Mechanical properties such as tensile and impact properties were tested from the hybrid and hybrid with EG containing PP compounds. Results for tensile properties are presented in Table I and Figures 1(a, b) and 2(a, b). Results for impact properties are presented in Table I and Figure 3(a, b).

Tensile Strength: Effect of Hybrid

Tensile strength results and modulus in Table I and Figure 1(a) are showing an increasing trend with increasing hybrid filler

content. The diverging result for 1% hybrid filler content with big variation in tensile strength may be due to a poor dispersion. Even though the result for 1% hybrid content is so deviating from others, it may indicate also real strengthening effect with very low amounts (<3% filler content) of hybrid filler if the material would only be properly dispersed. This strengthening effect is in line with the results found for pure CNT in other works and indicates identical behavior of composites with hybrid fillers or with pure CNT.⁸ Comparing a composite with 12% of hybrid (9% unit of CNT) and a composite with 10% CNT, the effect of these fillers on tensile strength is almost identical indicating about 13% increase in tensile strength. The variation to results is possible due to the small scale studied and the fact that, with mini-injection moulding equipment, all samples are manufactured separately. A detail is water content of

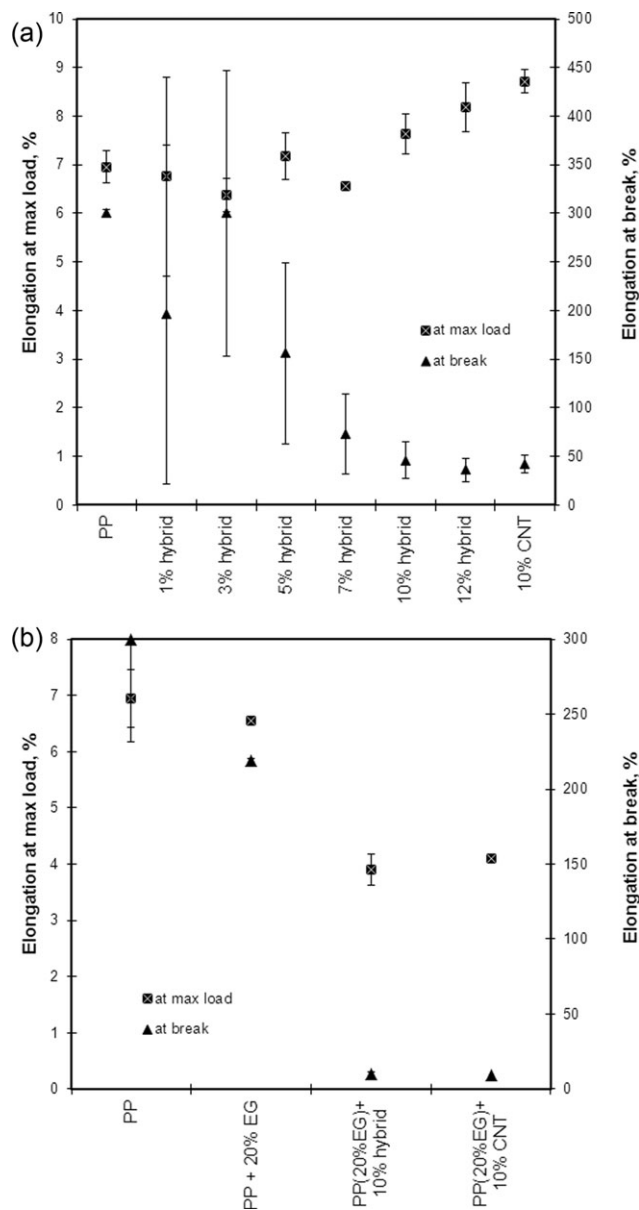


Figure 2. Elongation at maximum load and at break of composites with hybrid filler or CNT (a) and with EG and hybrid filler or CNT (b).

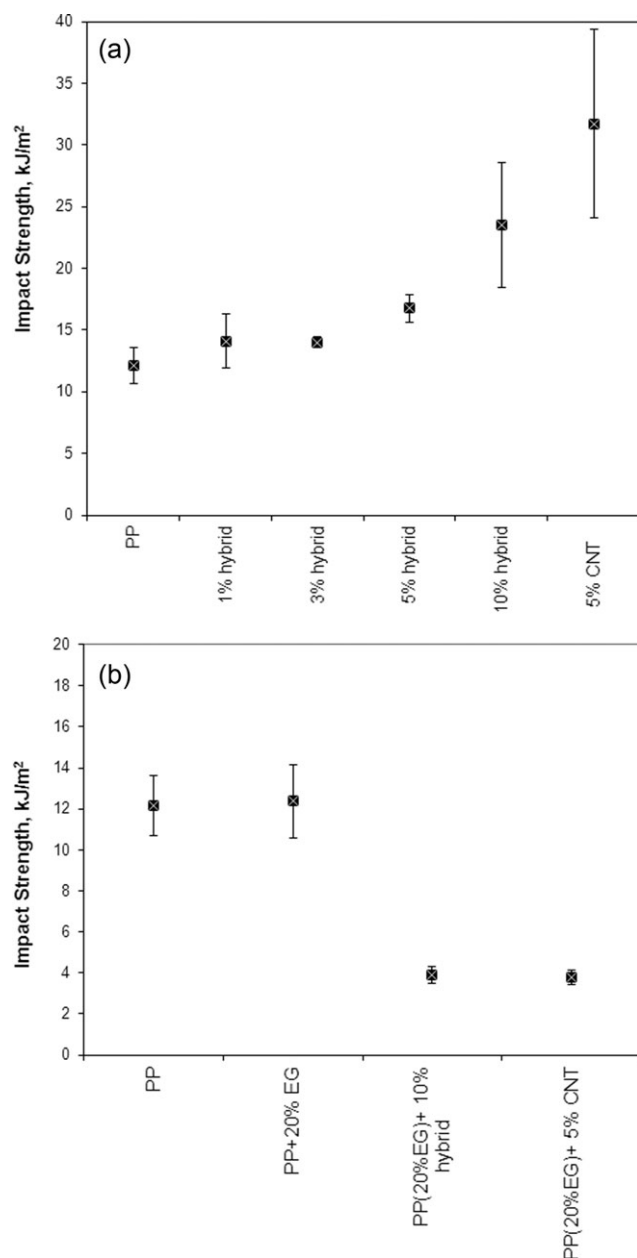


Figure 3. Impact strength of PP with hybrid filler or CNT (a) and the composites with EG (b).

hybrid, TGA analysis showed 97.4% dry solids content, and a small amount of PANi water can cause hydrolysis of EG which may modify mechanical properties of the compound.

Tensile Strength: Effect of EG in Hybrid Loaded System

In Table I and Figure 1(b) the addition of EG in PP lead to a weak, below 3%, decrease in tensile strength of PP. Composites with the dispersing agent (EG) and fillers (CNT or hybrid) have similar tensile strength values than without EG. Instead, the addition of 10% hybrid with EG to PP caused almost an 20% increase in modulus from the level of 1400–1800 MPa comparing with composites containing 12% hybrid (9 percentage units CNT) or with 10% CNT, those had quite identical modulus. Also the effect of EG addition to 10% CNT showed essentially

higher increase of modulus than without EG. This increase is almost 30% and indicates synergism between EG and carbon materials in toughening point of view, but cannot so clearly been seen in tensile strength. This may also be due to a better dispersion because of EG.

Elongation: Effect of Hybrid

Small addition (<7%) of hybrid filler resulted in a weak or insignificant decrease of the elongation at the max load. The addition of 10% hybrid to PP caused a below 10% increase of elongation as stated in Table I and Figure 2(a) indicating reinforcing effect in higher hybrid loadings. Instead the elongation at break, which is more related elastic properties of the material, dropped dramatically from over 300 to 36% at 12% hybrid loading.

Elongation: Effect of EG in Hybrid Loaded System

In Table I and Figure 2(b) the addition of EG in PP has no significant effect on elongation at the max load, but the addition of EG with both type of fillers (hybrid and CNT) caused an essential decrease of elongation at max load. In case of elongation at break, the phenomenon was more dramatic. When the elongation at break of neat PP was over 300%, values with about 10% of fillers were ~40%, but the simultaneous use of the dispersing agent (EG) with both type fillers the elongation at break collapsed below 10%.

These results emphasize the role of the coexistence of EG and CNT or hybrid filler in PP. In the earlier study of morphology, it was found that the EG was in a separate fibril-like phase.²³ The formation of this phase can be a reason for the observed dramatic ductile-brittle transition.

Impact Strength: Effect of Hybrid

Table I and Figure 3(a) present impact strength of PP compounds. According to these results, there was a remarkable toughening from 12 to 23.5 kJ/m² (93% increase) with 10% hybrid filler (containing ~7% unit of CNT) content and even higher, 260% increase, with 5% addition of pure CNT from 12 to 32 kJ/m². This indicates that the hybrid filler does not favour impact properties over the pure CNT. Above results indicate that the reinforcing effect was higher with pure CNT than with hybrid filler.

Impact Strength: Effect of EG in Hybrid Loaded System

Table I and Figure 3(b) show that the addition of 20% EG in PP did not have essential effect on the impact strength. The use of EG with hybrid or CNT collapsed the impact strength from over 20 kJ/m² to the level of 4 kJ/m² giving a sign of interactions between fillers and dispersing agent, which caused the material to become brittle. The impact behavior proves again the role of the phase of EG with fillers. An explanation of low elongation at break and low impact strength may be the nature of this phase; if in this phase fracture can easily nucleate, propagate fast, and expand like an avalanche by nucleating new propagating fractures in PP, the volume of influence of one particular fibril-like discontinuous phase is high. The result can be the fast total failure of the composite. Thus, to proof the hypothesis, the mechanism how fractures in EG-filler phase nucleate fractures in matrix should be considers and why EG itself is not able to produce this dramatic transition.

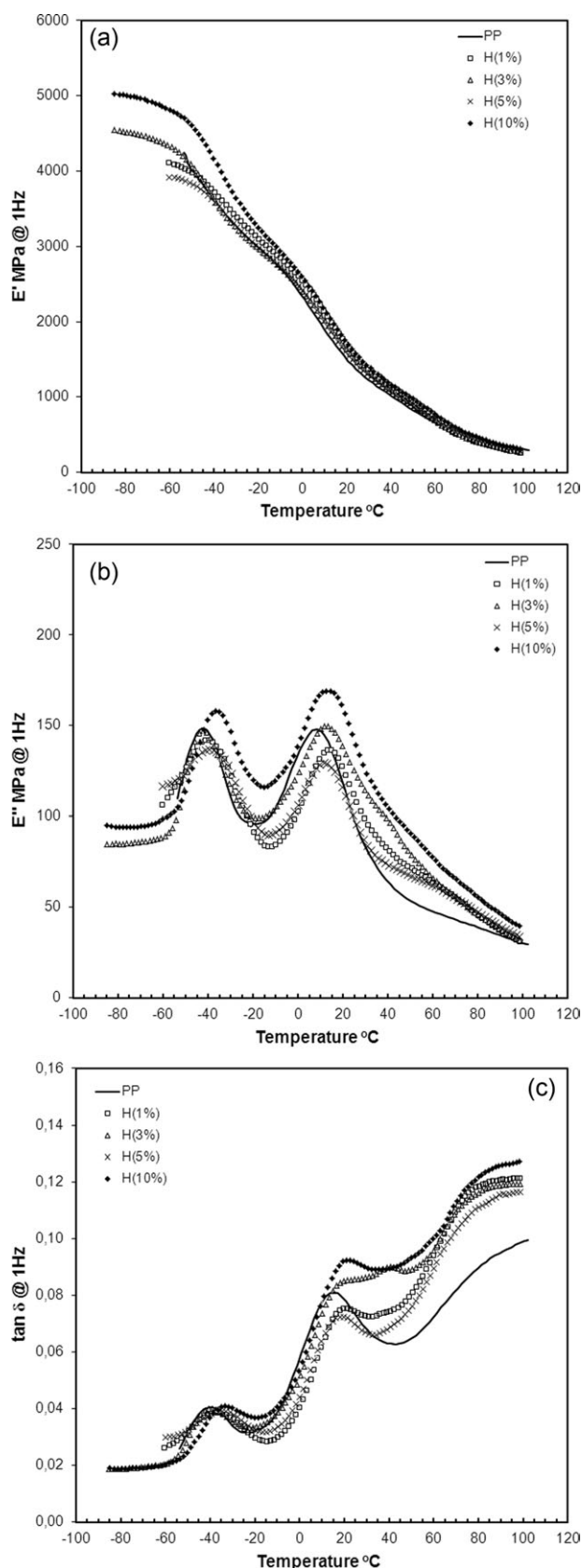


Figure 4. DMTA spectra of hybrid loaded PP composites, (a) storage modulus, (b) loss modulus, and (c) loss tangent.

DMTA

Effects of Hybrid Filler. To study effects of hybrid fillers in PP, dynamic mechanical properties were measured. Storage modulus for PP is typical for isotactic PP.¹⁷ Addition of hybrid filler in PP with low loadings does not have an essential effect on the storage modulus. The highest used filler loading, 10%, causes an improvement in the modulus which is clearly observable in the glassy region. Weak interaction between fillers and matrix, and poor dispersion lead to reduced modulus.

The mechanical loss modulus in Figure 4(b) gives information about relaxations in matrix. The loss modulus of neat PP shows γ and β transitions at temperatures -41.7 and 8.2°C , respectively. The neat PP does not show an observable sign of α relaxation. Table II presents peak temperatures of β and γ transitions. Addition of hybrid filler in PP by loadings of 1 and 3% does not significantly modify peak temperature of γ transition. The peak temperatures of these two composites and the neat PP are practically identical, -41.7 (± 0.7) $^\circ\text{C}$. By hybrid loadings of 5 and 10%, the peak of γ transition shifts to higher temperatures. The shift of the peak to higher temperatures is a result of restricted local motions in amorphous phase as a result of filler—polymer interactions.

Also peak temperatures of β transition, that is, large-scale cooperative motions in amorphous phase, are higher in hybrid composites than in the neat PP. Interactions between fillers and polymer chains restrict chain motions, and the result is a higher β peak temperature. These shifts do not show a systematic tendency as a function of the filler content, the highest peak temperature, 15.0°C , is measured by 1% loading and the lowest, 11.6°C , by 5% loading. The average β peak temperature of these four composites is 13.2°C which is significantly higher compared to the temperature of the neat PP. The filler dispersion can have a role in these unsystematic shifts.

In hybrid composites, α relaxation is observable in materials with 1 and 5% hybrid filler at a temperature about 60°C . Spectra of the composites with 3 and 10% hybrid loadings show a structure where the β relaxation peak has a high temperature shoulder. The shoulder is a result of the overlapping α and β transitions, but an open issue is the peak temperature of the

Table II. Relaxation Peak Temperatures Measured in Loss Modulus Spectra

Composite	T_γ [$^\circ\text{C}$]	T_β [$^\circ\text{C}$]
PP	-41.7	8.2
PP-EG	-42.4	15.0
PP H (1%)	-41.1	15.0
PP H (3%)	-42.4	13.5
PP H (5%)	-39.3	11.6
PP H (10%)	-36.7	12.8
PP-EG H (10%)	-35.1	20.3
PP CNT (5%)	-38.4	14.5
PP-EG CNT (5%)	-36.1	15.7

phenomenon causing this shoulder. A visual inspection of traces gives an impression of a peak occurring at a temperature lower than 60°C. If the origin of the relaxation is motions in crystalline phase, the increasing intensity of this relaxation may be a result of increased crystallinity and/or increasing amount of imperfect crystallinity.

The loss tangent in Figure 4(c) that is, the ratio of the loss modulus and the storage modulus, is usually reported and this data are used to define relaxation temperatures. Addition of hybrid filler causes minor variations in γ relaxation. The common tendency is the increase of the loss factor above the glass transition caused by α relaxation. Most of hybrid composites show a weak peak at about 40°C.

Effects of EG on Hybrid Loaded System. Addition of 20% EG in PP causes a remarkable decrease in the storage modulus, Figure 5(a). At the temperature range from -40 up to +40°C, the decrease is 10–20%. The phenomenon can be a plasticization effect of EG on PP or another straightforward explanation is that EG forms a separate phase in matrix as presented in the Ref. 23. The measured modulus is only the mechanical response of the neat PP and there is no load transfer over interface. This is the probable reason for decreasing modulus.

Compounding PP/EG/hybrid material where EG is added by the amount that the PP/EG ratio is 80/20 and the total amount of the hybrid filler in the composite is 10%, a strong improvement takes place in the storage modulus. This is a proof of dispersion ability of this kind of amphiphilic molecules. In this hybrid system, mainly PANi controls interaction between filler and the matrix. The result is expected before Ikkala et al.^{24,25} showed that the addition of selected esters of gallic acid favor the formation of a continuous PANi network in polyolefin blends. Between PANi and EG is proposed to exist molecular recognition. In our previous work, we used a group of gallates with different alkyl tail lengths and the highest conductivity, 26 S/cm, was measured in samples with EG which have the shortest alkyl tail in the gallate family.²³ Gallates with longer alkyl tail produce lower conductivities. Furthermore, the SEM micrographs showed phase separation in the composite.

The result of our work set a question what kind of mechanism creates the observed improvement in the storage modulus. If EG is able to create a good dispersion of hybrid fillers, the physical situation is similar what there exist, for example, in the case of PP-CNT composites. If EG is not able to disperse hybrid filler in PP due to its short alkyl tail, the composite is a biphasic system where hybrid filler and EG may form one phase due to their mutual interaction. To analyze interactions between this phase and the PP matrix, the amphiphilic nature of EG should be considered. The interaction between filler and EG can support the formation of a biphasic morphology. To reach observed increase in storage modulus, the modulus in the EG-hybrid phase should be high. If EG and the hybrid filler have tendency to form a mutual phase, the concentration of hybrid filler can be high in this phase where filler–filler interactions are present. This kind of a filler rich phase can explain high electric conductivity and some mechanical properties. Formation of nanofiller network may cause a sudden jump of storage modulus.^{17,27}

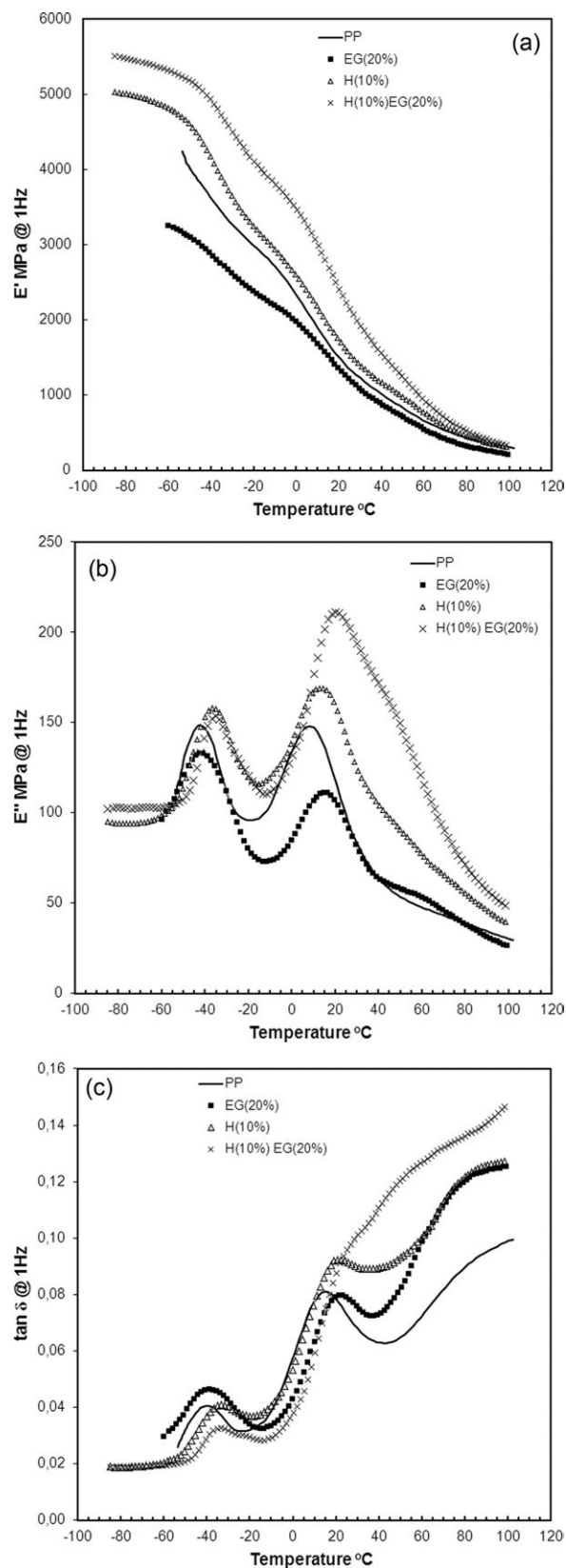


Figure 5. DMTA spectra of hybrid loaded composites with and without the dispersing agent, (a) storage modulus, (b) loss modulus, and (c) loss tangent.

Increased storage modulus caused by nanofillers is also explained by increased crystallinity nucleated by fillers.²⁸ More information is needed to give a detailed idea of the system.

The loss modulus of PP with 20% EG do not shows significant effects on the γ peak but the intensity of β relaxation decreases and the peak is sifted at a higher temperature compared to the neat PP, Figure 5(b). This hindered transition is on the contrary of normal plasticizing effects where the transition temperature shifts downward and the intensity increases. The observed phenomenon is similar to what many inorganic nanofillers produce in plastic compounds. EG is a crystalline organic material, thus, a question is: do crystalline EG inclusions have similar characteristic as many other nanoscale inorganic fillers have? A weak peak at a temperature $\sim 60^\circ\text{C}$ corresponding α transition is observable. EG inclusions have interactions on crystallization in PP.

PP-EG with 10% hybrid filler causes a significant increase in the γ peak temperature. The phenomenon can be linked with the existence of nanotubes in the composite. The composite shows an intensive β peak with a strong high temperature shoulder and the α peak temperature has shifted up to 20.3°C . The observed intensity and the temperature shift are high compared to PP composites with EG or with the hybrid filler. These phenomena are results of coexistence of the hybrid filler and EG in PP. The shape of the observed β peak is a sum of the separate peaks produced by α and β relaxations. If the intensity of the α peak increases, the result can be increased intensity of the β peak and simultaneously the peak temperature will shift to a higher temperature. Weidenfeller et al.¹⁴ reported simultaneous decrease of β and increase α as a result of nanoparticle addition. The phenomenon is explained by increasing crystallinity. The γ transition may disappear with high crystallinity and nucleating may vary crystalline form.¹⁵ Addition of nanotubes can cause observation of α peak.²⁹ The α process is presented to be intralaminar block motions in s-PP.³⁰ The result highlights the role of crystallinity in these composites.

The loss tangent shows minor effects of EG in hybrid loaded composite at γ relaxation temperature, Figure 5(c). $\tan \delta$ increases above T_g and the PP/EG/hybrid system shows continuous increase of $\tan \delta$ at the temperature range of $0\text{--}100^\circ\text{C}$ without a separate β peak. A typical phenomenon of fiber-reinforced composites is coexistent of increasing stiffness and decreasing damping. Reinforcing increases T_g values by the interactions between fiber and the matrix, which frozen molecular mobility, and by crystallinity.^{31,32} For the same reasons, damping values reduce. In this case, $\tan \delta$ do not decrease as a result of the filler loading. Chemical degradation causes usually strong improvement in β relaxation.³³ Broadening of β can be a result of increased inhomogeneous crystallinity.²⁸ Here, the observed damping behavior at higher temperatures is linked with the existence of α relaxation.

Effects of EG in PP/CNT System. To evaluate dispersing effects of EG for CNT, storage modulus of PP/CNT and PP/EG/CNT composites are presented in Figure 6(a). The addition of 5% CNT in PP increases the storage modulus, but the effect is

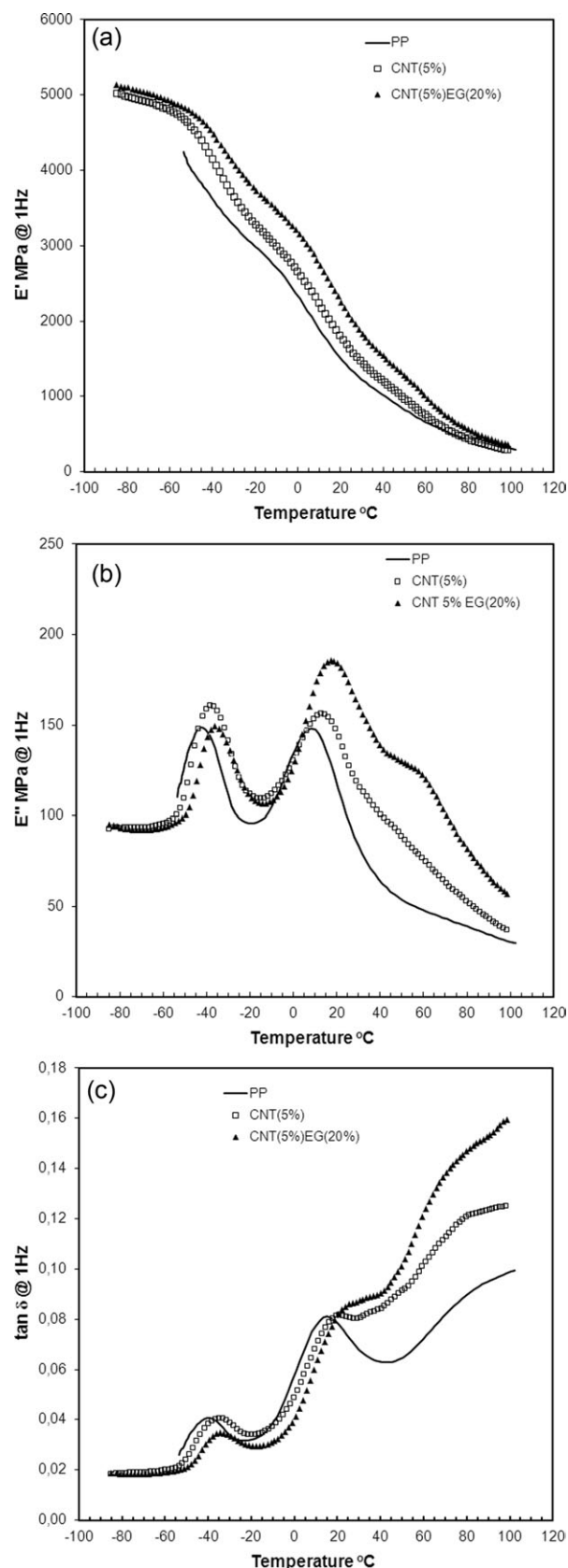


Figure 6. DMTA spectra of PP-CNT composites with and without the dispersing agent, (a) storage modulus, (b) loss modulus, and (c) loss tangent.

minor. The situation can be explained by poor dispersion and agglomerates of filler. Using EG in the composite, the higher storage modulus compared to the system without dispersing agent is observable. The effect is less remarkable what measured with the hybrid filler, but the ability of EG to disperse nanostructured carbon is evident. The aromatic ring structure dominates the both materials, CNT and PANi.

In the loss modulus, addition of CNT in PP shifts β and γ transitions at higher temperatures and α relaxation is observable, Figure 6(b). The β relaxation peak of PP/EG/CNT composite has a strong shoulder based on intensive α relaxation. The role of α relaxation in the observed intensity and peak temperature of β relaxation is evident. EG in PP/CNT composite increases $\tan \delta$ at high temperatures, Figure 6(c).

CONCLUSIONS

Organic–inorganic nanofillers offer a potential to realize high performance composites, such as excellent electric conductivity in plastic products. The hybrid concept allows tailoring interface of fillers to control interactions between filler and polymer matrix. Dispersing agents give an additional tool to engineer these systems. The *in situ* synthesized CNT-PANi hybrid filler is a candidate to produce conductive plastic compounds. A previous work highlighted the role of dispersing agents to realize high electric conductivity in PP with CNT-PANi hybrid filler. In this work, we have studied effects of an amphiphilic dispersing agent, EG, on mechanical and relaxation properties of CNT-PANi hybrid filled PP.

Tensile strength and modulus of hybrid filler and neat CNT filled composites were almost similar in higher filler loadings; however, indication of similar strengthening effect than in literature with pure CNT was found in low hybrid material content (below 3%). Addition of EG in PP matrix caused a weak brittle characteristic in the compound; tensile strength had a minor decrease but modulus increased about 25%. Addition of EG in CNT or hybrid filled systems had a remarkable effect on modulus which was about 30% higher compared to the composites without the dispersing agent. Elongation at maximum load and at break showed the brittle character of composites. Impact test repeated the same behavior. Addition of 20% EG in PP did not have an effect on impact strength, but CNT or hybrid filler with the dispersing agent showed very brittle behavior compared to neat PP or filler composites without EG.

Dynamic mechanical analysis repeated the observations of effects caused by EG in PP-hybrid composite. Using the dispersing agent in the composite caused a remarkable increase in storage modulus and also loss modulus increased, especially at temperatures above 20°C which may be a result of intensifying α relaxation. In PP-CNT composites, the role of EG was similar, although effects were less remarkable.

Addition of EG in CNT or hybrid-filled PP composites causes remarkable changes in mechanical properties which can observe as brittleness of composites and as intensive α relaxation. Detailed information about crystallinity and morphology is

required to verify the synergy of EG and fillers in PP composites.

ACKNOWLEDGMENTS

A part of this work has been carried out in European IP project POLYCOND (IP 515835-2) and Leonardo project iPolyCond, both partially funded by EC. The financial support is gratefully acknowledged.

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