



Optimization of Tribological and Mechanical Properties of Nanocomposites of Polyurethane/Poly(vinyl acetate)/CaCO₃

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Properties of samples containing polyurethane (PU), poly(vinyl acetate) (PVAc) and nanosize particles of calcium carbonate (CaCO₃) are correlated with concentrations of these components. Interphase phenomena in PU/PVAc/CaCO₃ nanohybrids have been studied before, we focus here on wear and scratch resistance. In addition to polymer blends containing CaCO₃, the effects of adding CaCO₃ with grafted PVAc, and CaCO₃ with grafted silane and PVAc in varying ratios are also evaluated. For blends that do not contain the filler, a hypothesis explaining the concentration dependence of friction called the Bump Model is advanced and supported by the experimental results. In particular, we explain how creating a blend containing only 10% of a second polymer results in a dramatic drop of friction of the majority polymer. In single scratch testing, above 3% the filler displays 'its own' resistance to scratching. Chemical modification of the filler results in shallower residual depths—a consequence of improved interaction of the filler with the polymeric matrix. In sliding wear determination, strain hardening is seen for blends as well as for filler-containing composites. In tensile testing, addition of an unmodified filler increases the elongation at break and thus lowers the brittleness; the effect is even larger for chemically modified fillers.

Keywords: Wear Resistance, Nanohybrids, Filler Reinforcement, Poly(vinyl acetate), Polyurethane, Calcium Carbonate Modification.

RESEARCH ARTICLE

1. INTRODUCTION

When considering composite materials for a predefined purpose, three most common classes of materials come to mind: metals, polymers, and ceramics. Metals, though the strongest of the three, are quite rigid. They also conduct electricity—what in certain applications can cause hazardous situations. A further disadvantage of metals is the fact that many are prone to chemical reactions with their environment (rust formation). Ceramics, unlike metals, tend to react less with environment. However, ceramics are brittle and also rigid and therefore have a limited scope of applications. Polymers, unlike the other two, generally have a high resistance to chemical reactions. They can be produced with a high malleability and high ductility, have low density, need little maintenance, and can be produced at relatively inexpensive prices. At the same time, polymers are weaker mechanically and tribologically (suffer from wear) than the other two major classes of materials.

In this situation, one provides reinforcement of polymeric materials to achieve improved mechanical and tribological properties. The traditional approach to reinforcement relies on creation of blends. We pursue that route also, namely by blending polyurethane (PU) with poly(vinyl acetate) (PVAc). However, we take a further step possible by inclusion of a filler with particle diameters in the nm range.¹ Various such fillers in use include silica, vanadia, metal particles as well as carbon nanotubes.^{2–13} More often is the formation of such nanohybrids for the purpose of *mechanical* reinforcement. Given the economical importance of *wear*, we provide particular attention to improvement of tribological properties—including mitigating wear, improving scratch resistance and also lowering friction. We apply techniques for determination of tribological properties used before.^{14–16}

We use as the filler CaCO₃ particles with diameters in the nm range. Due to their size, nanofillers have a large surface to volume ratio—what should lead to strong interfacial interactions among substrates. CaCO₃ has been used as a filler before, for instance for polypropylene + high density

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polyethylene blends.¹⁷ Thus, more parameters need to be evaluated than in usual blends: specific surface area of the filler phase, filler packing and surface activity, spatial distribution and ability of interactions of the filler with the polymer matrix.

Since interface interactions are inversely proportional to the size of the filler, decreasing the filler size would strengthen the interface interactions. One drawback to the use of nanoparticles as fillers is that, as the concentration of the nano-filler increases, the chance of agglomeration among the filler increases. A possible solution to reduce the formation of CaCO₃ agglomerates is the addition of silane. "Silanes have wide application as coupling agents between various types of fillers and matrixes, as well as primers in technology of bonding different materials. Reactive surface pretreatment of a filler with the silane coupling agent results in strong bonds between reactive groups of aminosilane with reactive groups of both filler and polymer matrix."¹⁸ The objective of this paper was to understand the influence of nano-CaCO₃ fillers with or without surface pretreatment on mechanical and tribological properties of the PU/PVAc/CaCO₃ nanohybrids.

2. EXPERIMENTAL DETAILS

2.1. Materials

Elastomeric PU was Desmocoll 176 (predominantly linear hydroxyl polyester PU, with weight-average molecular weight 1.0×10^5 g/mol, density 1.2 g/cm³) in the form of granules, provided by Bayer, Germany. We have used as vinyl acetate homopolymer Vinnapas B 60 sp (weight-average molecular weight 6.3×10^4 g/mol, density 1.18 g/cm³) in the form of granules, provided by Wacker Polymers, Germany. Precipitated calcium carbonate (PCC), Socal U1 (primary particle size 80 nm, specific surface area 20 m²/g, density 2.7 g/cm³) provided by Solvay, Germany, was the nanofiller. Commercial vinyl acetate monomer was used for grafting pretreatment without further purification. Silane pretreatment was carried out with 3-aminopropyl-triethoxysilane (ABCR GmbH & Co., Germany).

2.2. Sample Reference List

2.3. Sample Preparation

2.3.1. Filler Pretreatment

To produce CaCO₃-graft PVAc filler, the CaCO₃ nanofiller was preheated at 135 °C in an oven for 7 h to eliminate water possibly adsorbed on the surface of the particles. After that, a mixture of filler/monomer (100/40 by weight) and acetone as dispersion medium was agitated for 3 h. After the agitation, the mixture was irradiated by a ⁶⁰Co γ source at the dose rate of 1 Mrad/h at room temperature.

After the exposure to a dose of 4 Mrad, the acetone was recovered, and the filler was dried and grinded.¹ To produce CaCO₃-silane + graft PVAc filler, the CaCO₃ nanofiller was first pretreated with the silane and then with the PVAc. Details of the Socal U1 silane pretreatment procedure used in the present work have been described before.¹⁹

2.3.2. Composite Preparation

The polymer blends were prepared in a Brabender Plasticorder kneading chamber. First, the polymer granules and the filler were mechanically mixed, and then each blend was introduced into the Plasticorder chamber preheated to 140 °C and kneaded for 5–7 minutes with a rotor speed of 45 min⁻¹. The blends were prepared in 10/90, 30/70, 50/50, 70/30, and 90/10 PU/PVAc weight percent ratios. The content of CaCO₃ and pretreated CaCO₃ in the polymer blends was 3, 6, 12, and 18 wt%. After kneading, the polymer blend was cut into small granules and compression molded to 0.7 mm thick plates. The pressing temperature was 110 °C and the pressing time was 6–8 minutes. The plates were used for specimen preparation for morphological observations and tensile testing.¹

2.4. Friction Force Determination

Dynamic friction force was measured using the Nanovea pin-on-disk tribometer from Micro Photonics, Inc. We have used a steel 302 ball with the diameter 3.2 mm made by Saint-Gobain Ceramics. The conditions were 2.0 N, 3000 revolutions at 100 rpm, and we performed two trials for each sample at room temperature (22.5–23.0 °C). The machine measures the friction force between the probe needle and the surface of the substrate.

2.5. Scratch Resistance Determination

Scratch resistance was measured using a micro-scratch tester from CSM, Neuchatel, Switzerland, at room temperature (22.5–23.0 °C). A diamond indenter was used. The conditions for single scratch tests were 2.0 N, 5.0 mm scratch length at 5.22 mm/min, and 1 pass. We have also performed sliding wear determination by multiple scratching along the same groove following a technique applied before.^{2,3} We have applied the following parameters: 2.0 N, 5.0 mm scratch length covered at 5.22 mm/min, and 11 passes. We performed 3 trials for each single scratch and 2 trials to determine sliding wear. The initial or penetration depth R_p as well as the residual (recovery) depth R_n are measured. From these numbers the viscoelastic recovery f is calculated as

$$f = (1 - R_n/R_p)100\% \quad (1)$$

Table I. Composition of the composites.

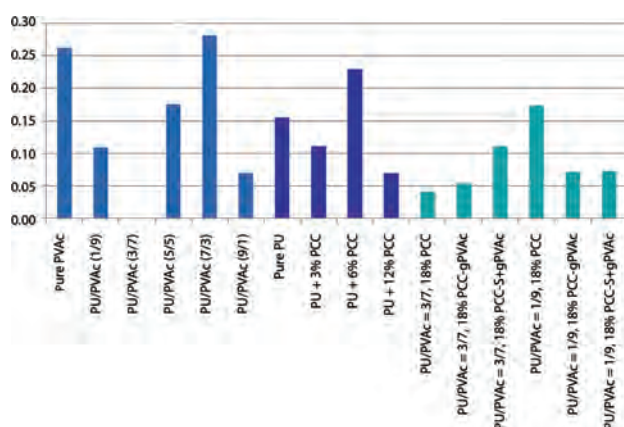
Sample name	PU/PVAc ratio in the composite	Wt% of polymers in the composite	Wt% of PCC in the composite	Filler pretreatment
Pure PVAc	0/100	100	0	—
PU/PVAc (1/9)	10/90	100	0	—
PU/PVAc (3/7)	30/70	100	0	—
PU/PVAc (5/5)	50/50	100	0	—
PU/PVAc (7/3)	70/30	100	0	—
PU/PVAc (9/1)	90/10	100	0	—
Pure PU	100/0	100	0	—
PU + 3% PCC	100/0	97	3	Untreated
PU + 6% PCC	100/0	94	6	Untreated
PU + 12% PCC	100/0	88	12	Untreated
PU/PVAc = 3/7, 18% PCC	30/70	82	18	Untreated
PU/PVAc = 3/7, 18% PCC-gPVAc	30/70	82	18	Grafted PVAc
PU/PVAc = 3/7, 18% PCC-S + gPVAc	30/70	82	18	Silane + grafted PVAc
PU/PVAc = 1/9, 18% PCC	10/90	82	18	Untreated
PU/PVAc = 1/9, 18% PCC-gPVAc	10/90	82	18	Grafted PVAc
PU/PVAc = 1/9, 18% PCC-S + gPVAc	10/90	82	18	Silane + grafted PVAc

2.6. Mechanical Properties

Tensile properties (strength at break, elongation at break, elastic modulus and work to break) of our nanohybrids were determined using a Zwick 1445 universal testing machine at 23 °C; the crosshead speed was 25 mm/min and the gauge length was 40 mm.

3. FRICTION RESULTS

Figure 1 shows the results for the averages of the dynamic friction force. A key parameter here is the effective contact area. That area can be smaller than the nominal surface area—the latter usually calculated assuming a flat ideally planar surface. Consider first the results on the l.h.s. of the diagram, from the PU/PVAc ratio 0/100 up to 100/0. Starting from the left side, addition of 10 wt% of PU results in significant lowering of friction. At 0/100 the pin was moving on a flat surface of pure PVAc. Moving to the 1/9 composition results among others in appearance of little bumps of PU protruding from the predominantly PVAc

**Fig. 1.** Average results for dynamic friction force.

surface. The pin now moves ‘jumping on’ the bumps and touching less the PVAc matrix surface. Indeed the effective surface area is much smaller than the nominal planar surface area. The result is dramatic; the dynamic friction force is *less than one half* of the value for pure PVAc. Let us call the explanation just provided the Bump Model. Now, when we increase further the concentration of the polyurethane, the PU regions become larger areas on the surface, not small bumps anymore.

Let us now go to the other end of the concentration scale, pure PU or 100/0. We now move from this composition towards 9/1, so that 10% of PVAc is present. If our bump model is correct, then small bumps of PVAc on the predominantly PU surface should cause a large reduction of dynamic friction. This indeed is the case, the dynamic friction *also here is less than one half* of the value for pure polymer. Our model has been verified at both ends of the concentration range.

Finally, we consider a region centered around the middle of the concentration range. The pin moves over large areas of PU and also over large areas of PVAc. Each of these components makes its own significant contributions to the overall friction. Moreover, moving from a region of one of the constituents to a region of the other means moving over a ‘border.’ The border makes the movement of the pin more difficult; now the indenter moves across the entire surface of each region. The indenter is not just jumping from bump to bump as it was doing before—then with little contact with the surface between the bumps. A high friction results, in fact even higher than friction values for pure components. The maximum value is not in the middle of the concentration range. Since neat PVAc has a much higher dynamic friction than neat PU, addition of 30% PVAc to PU results in the highest dynamic friction value overall.

A brief comment on effects of PCC seems in order. Addition of 3 wt% PC to PU results in lowering of dynamic

friction. However, addition of 6% results in the friction value higher than for pure PU. These results can also be explained by the Bump Model. At 3% we have small bumps of PCC, thus lower friction values. At 6% PCC we have appearance of PCC regions and thus the difficulty already noted when the indenter moves from a PU-rich region to a PCC-rich region across a ‘border’ between the two. Then we have a quite interesting result for 12% PCC: the lowest dynamic friction in this set of four materials. Apparently when the indenter is moving inside of PCC ‘islands’ now larger than before, PCC offers low resistance to movement; overall low friction is the result.

4. SINGLE SCRATCHING RESULTS

We present the results in Figure 2.

We see in Figure 2 that polymer blends with high concentrations of PU have high penetration depth values.

Values of the penetration depth and percentage recovery characterize viscoelastic character of our materials. Addition of 3% nanofiller to PU results in a slight increase of the recovery; possibly the cohesive structure of the polyurethane is disrupted by the presence of CaCO₃. The result is an increase in free volume,^{20–22} thus enhanced mobility of the chains and more recovery. However, a further addition of the nanofiller—which by itself is not viscoelastic—necessarily lowers the values of f defined by Eq. (1). The effects are not large, however.

A somewhat related argument applies to the effect of the presence of CaCO₃ on the residual depth. Adding just

3% of the filler to PU causes a dramatic decrease of residual (healing) depth R_h . Thus, above 3% the filler displays ‘its own’ resistance to scratching. This effect still increases for 6 and 12% of PCC. That last composition has very shallow residual depth. Chemical modification of the filler does *not* result in shallower residual depths—a consequence of stronger interaction of the filler with the polymeric matrix; now the matrix and the filler act more in unison.

5. SLIDING WEAR RESULTS

Sliding wear results obtained as before by repetitive scratching along the same groove²³ are presented as residual depth for selected compositions in Figure 3.

Above all, we see in Figure 3 that the materials display strain hardening in sliding wear—discovered originally in 2004.²³ That is, at some point consecutive passages of the indenter do not cause deepening of the groove any more. This has been explained before by first increased surface area of contact of the indenter and then by densification of the material at the bottom and walls of the groove.^{24, 25}

Pure PVAc had a shallow residual depth in single scratch testing. This situation prevails also in sliding wear determination.

6. MECHANICAL PROPERTIES

We present in Figure 4 stress σ versus strain ϵ results for blends without the filler.

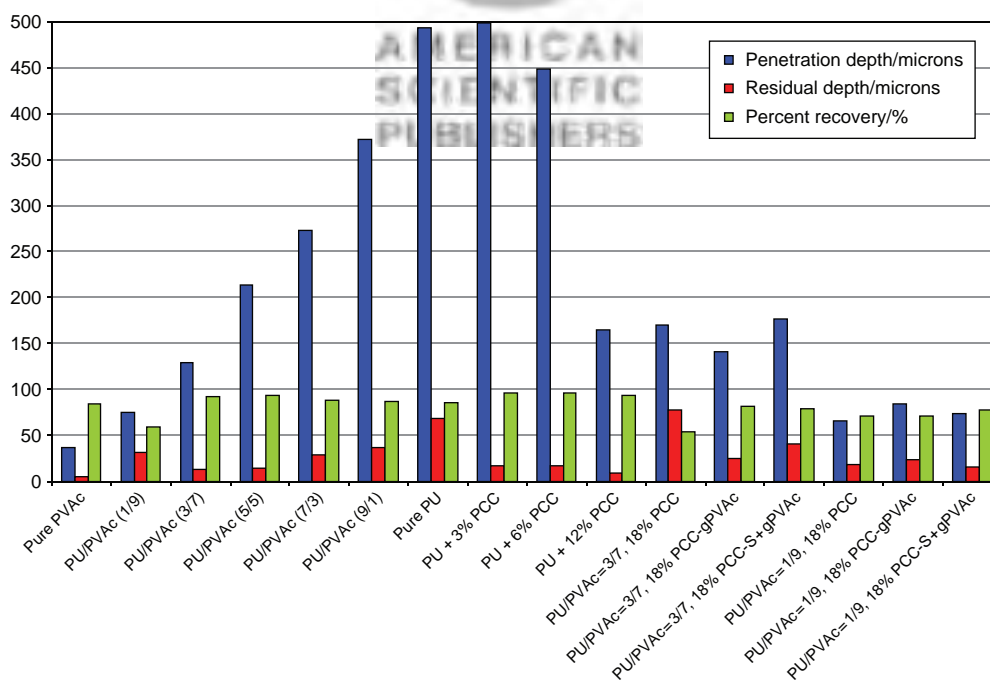


Fig. 2. Single scratch testing results.

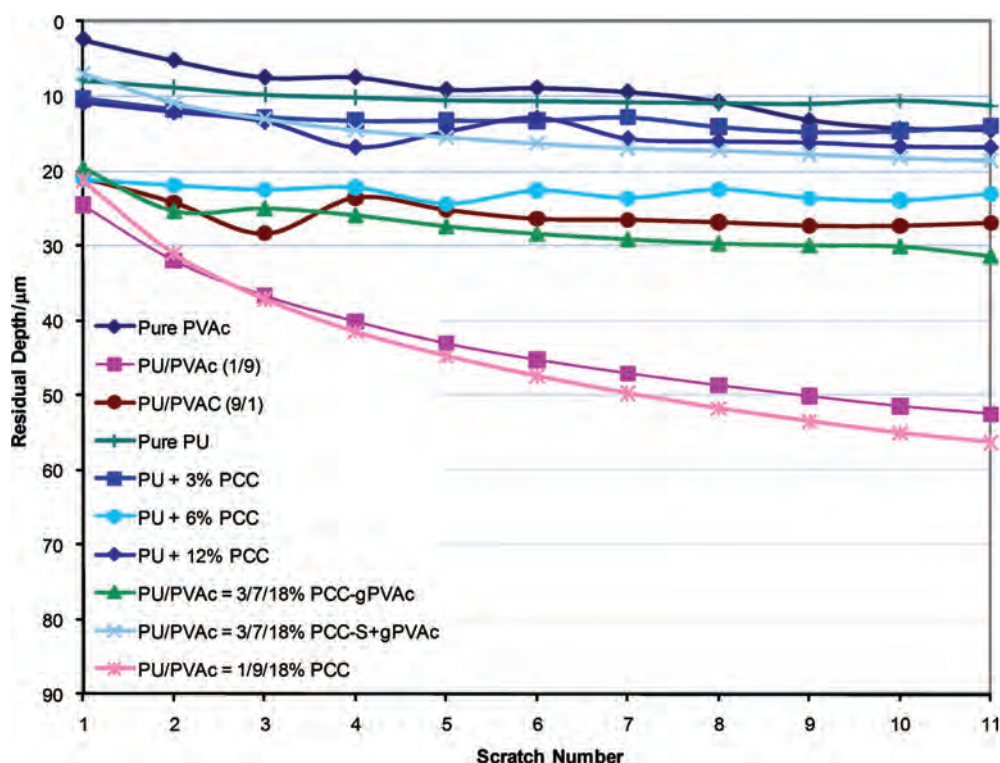


Fig. 3. Residual depth as a function of the number of scratches.

We see that pure PVAc has the shortest elongation at break ε_b by far (the black nearly vertical line). We recall that the material brittleness B is inversely proportional to ε_b .²⁶ Inclusion of 10% PU changes this situation only slightly (red line). 30% of elastomeric PU provides a more typical curve. Next in terms of increasing ε_b is pure PU (dark blue line). Curves for 90% and 50% PU follow. The highest elongation at break is seen for 70% PU (green curve); high extensibility of PU is aided here by disruptions in the neat PU structure caused by the presence of 30% PVAc.

Impact of filler addition on the polymer blend mechanical properties is shown in Figures 5 and 6.

We see in Figure 5 that—compared to the pure PVAc and PU/PVAc (1/9) polymer blend without filler—the blend with 18% of filler has a larger elongation at break. The filler modification results in a still higher ε_b . Apparently, enhanced interaction of the filler with the matrix produces this effect. Kopczyńska and Ehrenstein²⁷ note the importance of interfaces for properties of multiphase composites.

Consider now the results for PU/PVAc (3/7) without and with a filler in Figure 6. Here, the filler significantly increases the elongation at break ε_b while it also much reduces the stress at break σ_b . With three times as much of the elastomeric component as in Figure 5, and the filler clearly well ‘cooperating’ with PU, we have ε_b not far from 500%, nearly twice the value without filler.

It is a well known fact that a finely dispersed elastomer is able to improve polymer toughness.¹ In our polymer blends, the adding of elastomeric PU enhances strength and elongation at break (Fig. 4). It should be noted that the PU/PVAc (5/5) material shows very low strength at break (Fig. 4) compared to all other samples in spite of the fact that the two polymers are completely miscible, what was confirmed by DSC analysis.¹ This result corroborates that inference that the best mechanical properties will not occur in completely miscible polymer blends. In other words,

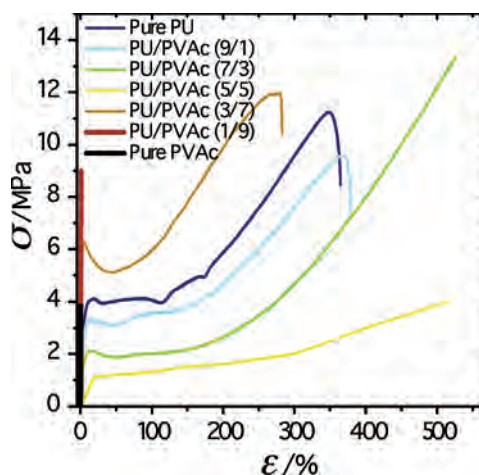


Fig. 4. Representative stress–strain curves for PU, PVAc and their blends.

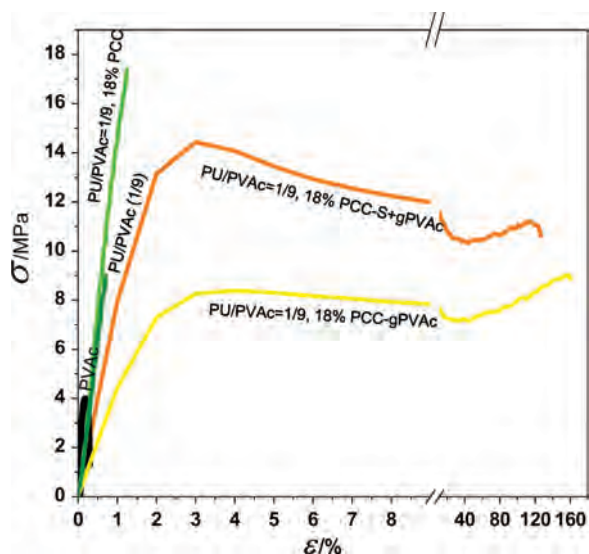


Fig. 5. Representative stress–strain curves for PVAc and 1/9 PU/PVAc polymer blends without and with 18% of untreated U1 and pretreated CaCO₃-graft PVAc filler and CaCO₃-silane + graft PVAc.

some phase dispersion has to remain in order to achieve good mechanical properties.

Adding of PVAc to the PU matrix improves mechanical properties of the polymer blend with the maximum in the PU/PVAc 7/3 material; thus, we can tailor properties of PU adhesives by adding PVAc and thus also lower the final product price. Adding of PU to the PVAc matrix also enhances the strength at break of the samples. At the same time, also elongation at break increases; for this reason plasticizers for enhancement of the elasticity are not needed.

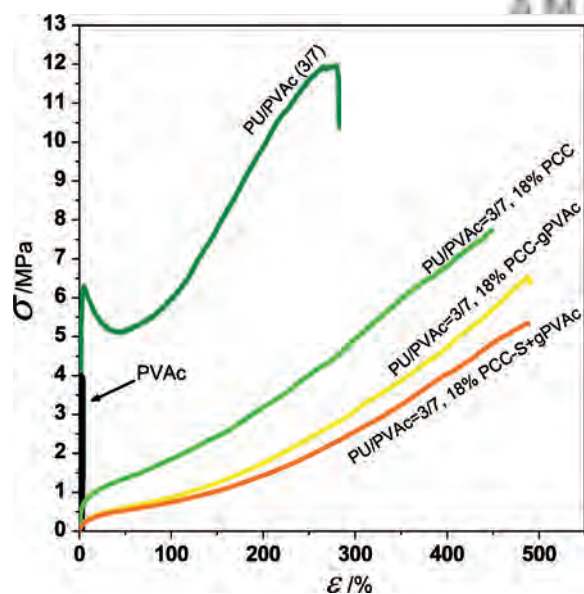


Fig. 6. Representative stress–strain curves for PVAc and 3/7 PU/PVAc polymer blends without and with 18% of untreated U1 and pretreated CaCO₃-graft PVAc filler and CaCO₃-silane + graft PVAc.

7. CONCLUDING REMARKS

Reasons for the increasing use of polymer-based materials have been discussed in the beginning of this paper. We have found that the addition of CaCO₃ nanofiller can reduce friction significantly. The filler also increases the elongation at break, an effect enhanced by chemical modification of the filler. Our results will allow extension of applications of polyurethane adhesives. Polyurethanes have a large variety of applications,^{28–34} not only on land but even in seawater.^{33,34}

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