Characterization of the Dynamic Properties of Binary Polypropylene Blends via the Hysteresis Measurement Method

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SUMMARY: Due to the poor impact behavior of polypropylene (PP) at low temperatures, blending PP with an elastomeric phase is a common way to improve some of the characteristic quantities. The property profile of thermoplastic elastomers strongly depends on the content of the elastomeric component. For applications under dynamic loading conditions, the corresponding material behavior is of importance. In order to reduce long testing times with constant amplitude loading, the hysteresis measurement method, which evaluates the hysteresis loop and makes use of a stepwise load increase procedure (SLIP), was developed. Binary blends based on PP were compounded with either ethylene-propylene-dien-rubber (EPDM), metallocene polymerized polyethylene (mPE), or styrene-ethylene-butylene-styrene block copolymer (SEBS) as the elastomeric phase. Static and dynamic tests under tensile and pressure conditions were performed in order to evaluate the influence of the type of elastomeric phase on the properties of these blends. It is shown how the hysteresis measurement method can be used to determine dynamic load limits for the application of these blends and of other polymers. Some properties improved slightly when using mPE.

Introduction

It is well known that fracture toughness of PP is poor when exposed to low temperatures. One method which may be used to increase the fracture toughness is by decreasing the glass transition temperature via copolymerization, e.g. with ethylene. Unfortunately, this can only be done within a reactor, thus the material processor cannot influence the properties of the material by this method directly. Therefore, compounding PP with a dispersed elastomeric phase e.g. EPDM is widely used. The rubber increases the overall toughness of the PP matrix[1)] and lowers production costs. Another benefit of blending, preferably using a twin-screw extruder, is that a wide range of mechanical properties are achievable.

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The development of metallocene catalysts has lead to numerous new polyolefinic materials with mechanical properties previously unknown with conventionally polymerized polyolefins. Metallocene polymerized polyethylene (mPE) polymerized with octene as a copolymer possesses a very homogeneous copolymer distribution and a narrow molecular mass distribution. In comparison to EPDM, it has been found that mPE can accomplish higher knit-line impact strength[2)] as a modifier of PP.

Also of interest is the use of styrene-(ethylene-butylene)-styrene tri-block copolymers (SEBS) as the elastomeric phase[3)]. However, for all mentioned types of modifiers it is necessary to know the mechanical properties of the blend when using only a relatively simple compounding process. The present paper describes the influence of different blend compositions on the dynamic material properties using the hysteresis measurement method.

The Hysteresis Measurement Method

In classical fatigue tests, the specimens are subjected to cyclic loading, the number of cycles to failure is monitored, and the results are presented as S-N curves (stress vs. number of cycles to failure). Usually a stress limit exists below which fatigue failure does not occur before 10^6 - 10^7 cycles. This stress is often defined as an endurance limit. However, the information retrieved from S-N curves do not indicate any structural changes during the fatigue process.

Compared with the common S-N testing approach, the hysteresis method has two fundamental advantages in characterizing dynamic material properties[4)]: more information on the fatigue process itself, i.e. structural changes, and a decrease in the test duration using a special test procedure. The increase in information is comparable to a situation where a stress-strain diagram becomes available instead of only a single data point, e.g. maximum stress or strain from a non-instrumented tensile test. This improved knowledge of the fatigue process becomes important as soon as the safety of the operation of a part depends on maintaining a certain stiffness or geometry, and actual part breakage does not occur. The method has already been successfully applied to various thermosets and thermoplastics[4)].

Under cyclic loading, hysteresis loops as shown in Fig. 1a) are induced by the viscoelastic material behavior and by material damage. The difference in shape between the ideal (Fig. 1a) and real hysteresis loop (Fig. 1b-d) results from non-linear viscous and frictional damping in the material, whereas the shift of the loop origin is due to relaxation and retardation. These loops can be evaluated by calculating four different characteristic quantities: stress ,σ; strain, ε; modulus, E; and mechanical energy, w. Relevant basic properties are the dynamic modulus, E_{dyn}, as a quotient of the stress and the strain amplitude (σ_u, ε_u: upper stress and strain, respectively; σ_m, ε_m: mean stress and strain at mean stress, respectively; σ_l, ε_l: lower stress and strain, respectively; σ_{mc}: mean stress curve), Fig. 1:

$$E_{dyn} = (\sigma_u - \sigma_l) / (\varepsilon_u - \varepsilon_l) \tag{1}$$

and the damping factor, Λ, as the quotient of loss energy, w_l, and strain energy, w_s:

$$\Lambda = w_l / w_s \tag{2}$$

The stiffness ratio of the upper and the lower modulus, E_u and E_l respectively,

$$E_u / E_l = \tan\alpha_u / \tan\alpha_l \tag{3}$$

is another very useful quantity to determine changes in the loop shape e.g. with thermoplastic elastomers[5)].

For the hysteresis measurement method, two test procedures were used. The Stepwise Load Increase Procedure (SLIP) increases the dynamic load after a certain number of cycles while the load ratio remains constant. This enables the rapid determination of load dependent quantity changes. Time dependent changes in characteristic quantities are monitored by the Single Load Level Procedure (SLLP) where load amplitude and load ratio remain constant, comparable to the common procedure for S-N curves. The load ratio, R, is defined as:

$$R = \sigma_l / \sigma_u \tag{4}$$

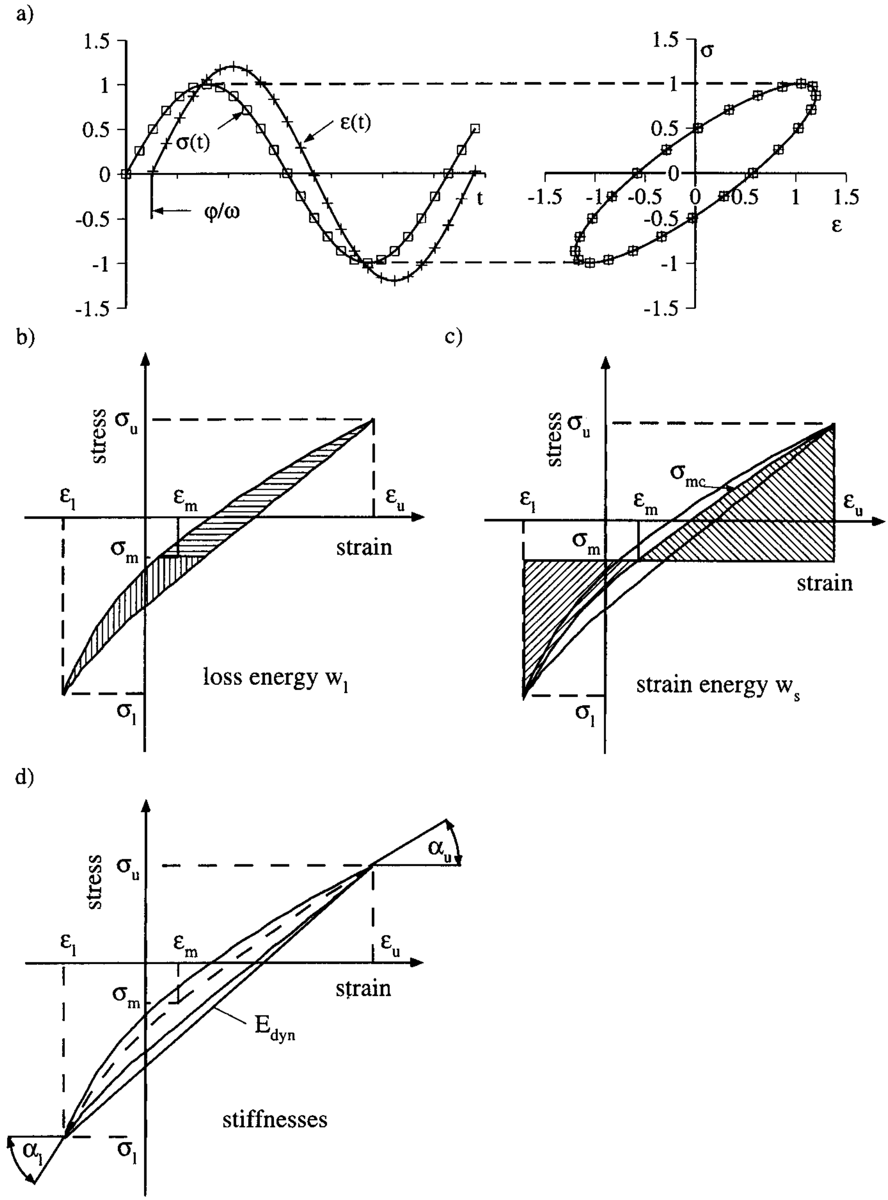

Fig. 1: a) determination of an ideal hysteresis loop and b-d) characteristic quantities as derived from the hysteresis loop (different patterns denote upper and lower energies, definition of quantities in text).

Experimental

Materials and sample preparation

The experimental examinations incorporated a block-copolymer PP (Vestolen P9500, DSM) as the matrix material. A twin screw extruder (Leistritz LSM 30/34 GL, mass temperature: 200°C, turning speed: 75/min) was used to blend the PP with either semicrystalline EPDM (Buna AP 437, Bayer AG), mPE (Engage EG 8150, DuPont Dow Elastomers S.A.), or SEBS (Thermolast K TC 8AAB, Gummiwerk Kraiburg GmbH).

The elastomeric component was added in amounts of 25, 40, 60, and 80% by weight. After compounding, the blends were injection molded into flat plates (115mm x 115mm x 6mm) using a mass temperature of 200°C and a mold temperature of 40°C. The experimental specimens were machined from these plates parallel to the flow direction. The specimen geometry, shown in Fig. 2., allowed for both creep and dynamic experimental investigations. The ability to use the same geometry for both tests allows for a correlation of the material behavior under different loading situations not influenced by the specimen geometry.

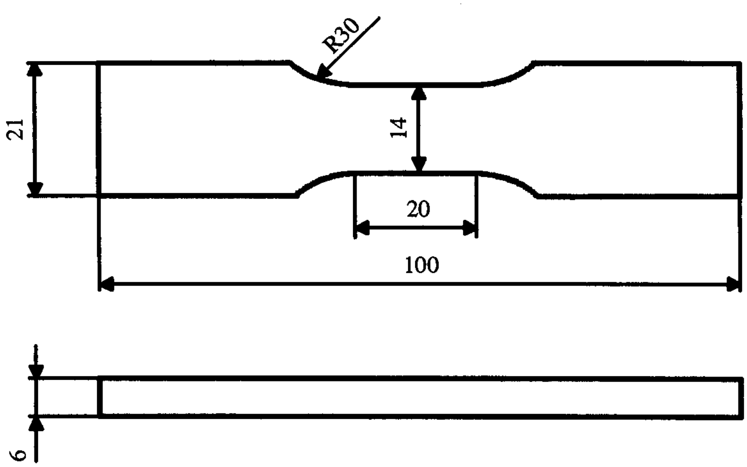

Fig. 2: Sample geometry (dimensions in mm).

Testing equipment and procedures

All mechanical tests, except for the Charpy fracture toughness test, were performed at a temperature, T, of 23°C and 50% relative humidity. Tensile tests for the mechanical characterization of the material were conducted on a Zwick 1465 testing machine using a crosshead speed, v, of 200 mm/min.

In order to determine the response of the material under high speed loading, two types of tests were implemented. Charpy notched impact strength at -40°C (standard testing temperature in the automotive industry) was measured for the evaluation of the effectiveness of the different elastomeric components in increasing the fracture toughness of PP. The energy absorption, i.e. the damping of the material, is often characterized by the rebound resilience. These data were determined using a Hampden EPH-50 elasticity tester.

Tension-tension fatigue testing was performed on a Schenck servo-hydraulic testing machine. A load cell and an extensiometer measured the time dependent force, F(t), and longitudinal elongation, l(t), for the calculation of the hysteresis loops (Fig. 3), respectively. The specimens were subjected to a stress controlled sinusoidal oscillation. The frequency, f, during testing was 0.35 Hz in order to avoid hysteretic heat up of the samples. SLIP was carried out in order to obtain load limits for dynamic loading. The stress was kept constant during a period of 250 cycles and then set to the next higher level. SLLP showed the validity of the resulting load limits by exhibiting constant characteristic quantities if loaded below the limit and increasing/decreasing quantities above the limit.

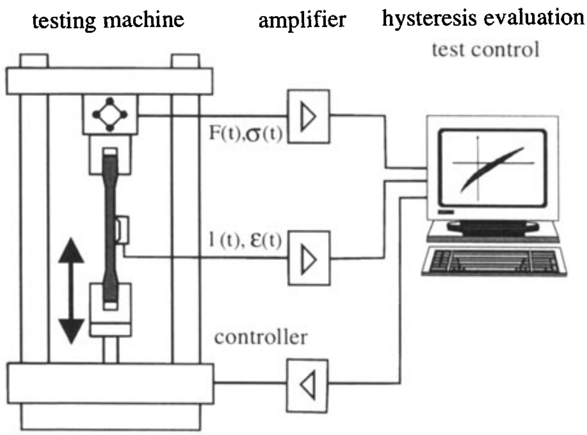

Fig. 3: Test configuration.

Results and Discussion

Tensile Tests

In Fig. 4, the modulus and yield strength, measured via static tensile test, are shown in dependence on the content of the elastomeric component. As expected, the modulus and yield strength decreases as the elastomer content increases, while elongation at break also increases. Since the blends with more than 60% soft phase did not show a definite yield point, a tensile stress at the 2% offset yield point was determined. Considering the calculated standard deviation, there was not a significant difference between the modulus of the different elastomeric components for equal composition, whereas yield stress and elongation at break showed a component dependent behavior. For the given processing parameters, the yield strength of the SEBS-blends came closest to the linear mixing rule, in spite of two different ways of quantity determination. Concerning the elongation at break, the PP/SEBS-blends showed better properties at 23°C than PP blended with one of the other two elastomeric components, with PP/EPDM having the most favorable response as shown in Fig. 5.

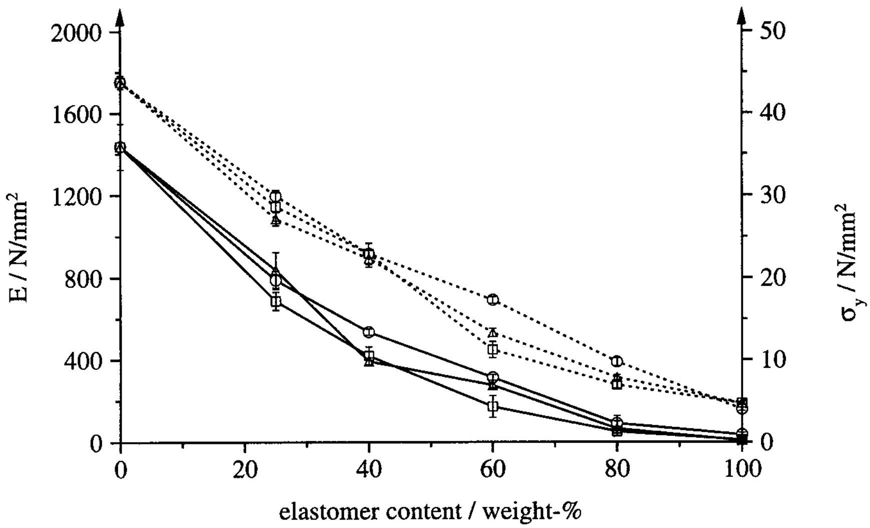

Fig. 4: Modulus E (---) and yield strength σ_y (—) as a function of elastomer content; tensile test: T = 23°C, v = 200 mm/min; ○ = PP/SEBS, □ = PP/mPE, △ = PP/EPDM.

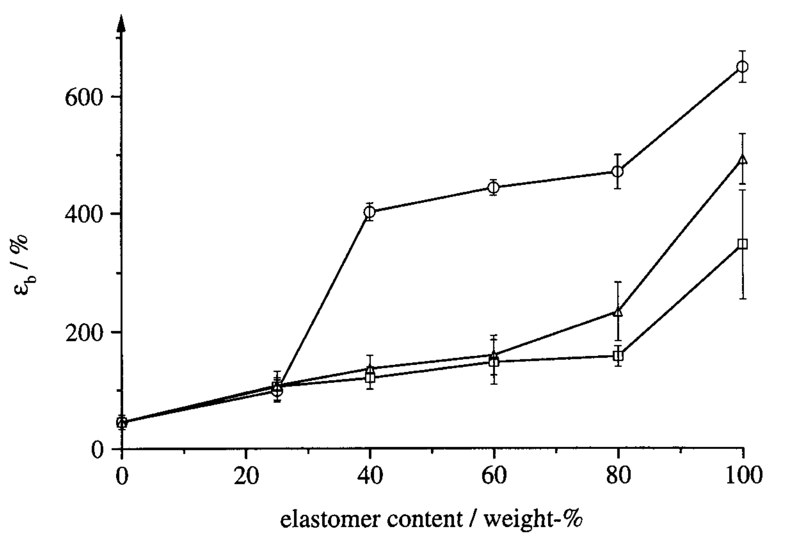

Fig. 5: Elongation at break ε_b (—) as a function of elastomer content; tensile test: T = 23°C, v = 200 mm/min; ○ = PP/SEBS, □ = PP/mPE, △ = PP/EPDM.

Impact Strength

The Charpy notched impact strength determined at -40°C is shown in Fig. 6. It can be seen that the examined mPE grade was the most effective modifier to increase the toughness of the PP at low temperatures when compared to the other types of elastomeric components. A significant increase in impact strength was becomes apparent at a composition of 25% elastomer. With 40% mPE, these samples did not completely break, with 80% mPE they did not break at all. In the case of EPDM, 60% was necessary to obtain a hinge failure, whereas complete rupture occurred with a composition of 80% SEBS.

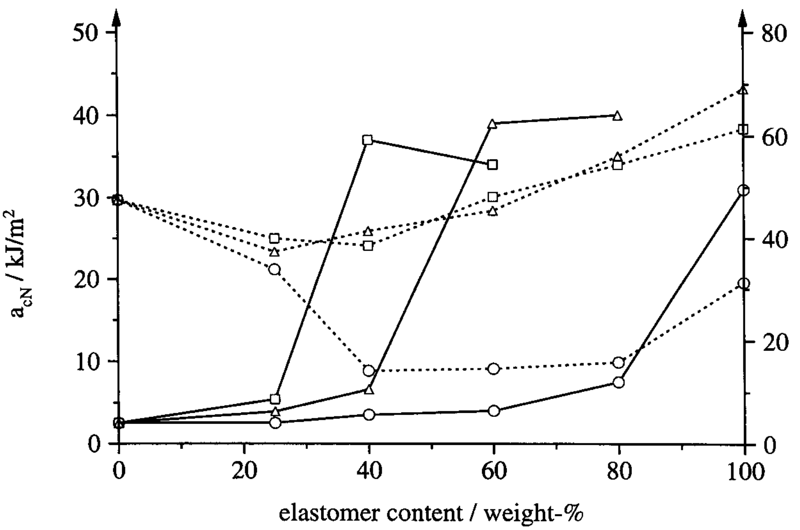

Fig. 6: Charpy notched impact strength a_{cN} (—) at T = -40°C and rebound resilience RR (---) at T = 23°C as a function of elastomer content; ○ = PP/SEBS, □ = PP/mPE, △ = PP/EPDM. (a_{cN} > 20 kJ/m² => hinge fracture, no value => no fracture)

Rebound Resilience

The rebound resilience at 23°C is also shown in Fig. 6. As in static tensile tests measured at room temperature, the SEBS-blends showed some advantages as far as energy take-up at compositions of more than 25% elastomer. On the other hand, no differences were found in the damping of PP/mPE- and PP/EPDM-blends.

Dynamic Experiments

Fig. 7 shows the characteristic quantities of the hysteresis measurements on specimens with a 40% elastomer content (stress, strain, and damping diagrams show upper, mean, and lower values). The dynamic modulus exhibited a decrease with the use of EPDM much faster than with mPE. Thus, in spite of the higher modulus of the PP/EPDM-blend at the beginning of the test, the mPE-blend maintained the dynamic properties up to higher load levels. It became evident that the PP/EPDM-blend entered a region of exponential increase in strain and modulus ratio earlier, i.e. the PP/mPE-blend had a higher dynamic load limit.

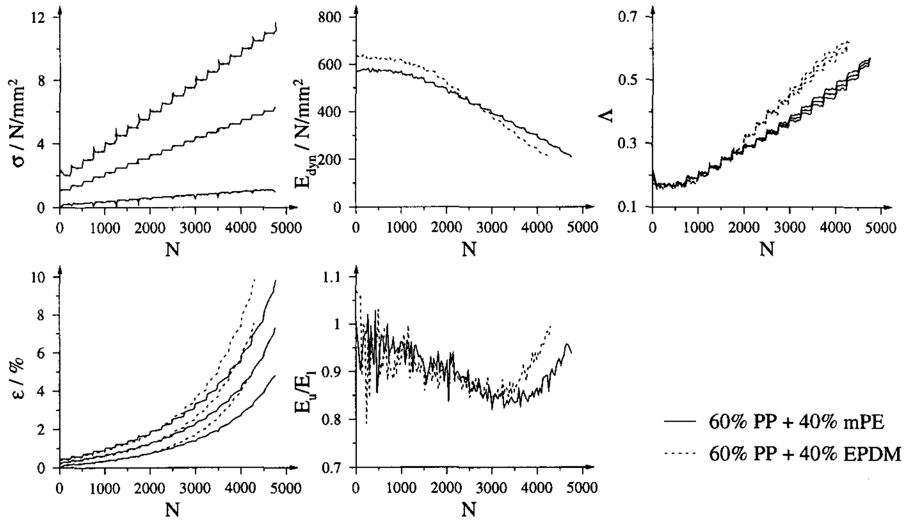

Fig. 7: Behavior of the binary PP-Blends with 40% EPDM and with 40% mPE content; SLIP at 23°C and 50% relative humidity: f = 0.35 Hz, R = 0.1.

The decrease of the determined load levels, σ_Λ, at which exponential changes of the damping values (or the stiffness ratio, if occurring earlier) were observed, is shown in Fig. 8 as a function of the elastomer content. The PP matrix dominated the dynamic deformation behavior of the blend upp to a content of 25% elastomer. At higher contents of mPE, slightly higher dynamic load limit were observed for EPDM and SEBS at equal compositions.

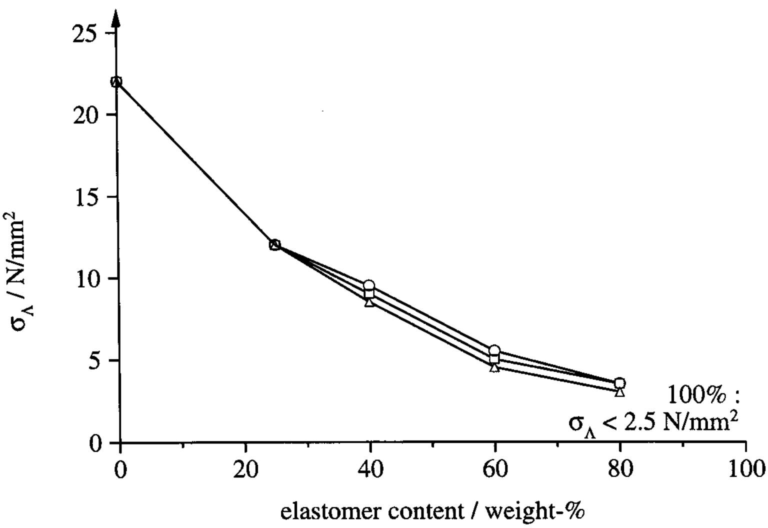

Fig. 8: Critical dynamic stress σ_A (—) as a function of elastomer content; SLIP: T = 23°C, v = 200 mm/min; ○ = PP/SEBS, □ = PP/mPE, △ = PP/EPDM.

Conclusions

The fracture toughness of the PP exhibit an increase at low temperatures when compounded with mPE, EPDM or SEBS. At equal compositions, the PP/SEBS blend showed slightly higher static quantities at room temperature. In addition, the energy take-up, as represented by the rebound resilience, performed better for the PP/SEBS blend than for blends with the two other types of elastomeric components. However, as far as fracture toughness at –40°C and dynamic behavior at 23°C are concerned, the PP/mPE blend showed a higher efficiency, and superior critical load limits, respectively. At room temperature, no significant differences in the static quantities between mPE- and EPDM-blends were observed.

The hysteresis measurement method was successfully applied to determine dynamic load limits, characterized by non-proportional quantity changes. Thus, the blends could be continuously evaluated with respect to their deformation behavior and dynamic properties. The optimizations of the mechanical properties by adjusting process parameters and an evaluation of the behavior at different frequencies and temperatures have to be investigated in further studies.

Acknowledgements

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References

1. J. Karger-Kocsis (Ed.), *Polypropylene - Structure, Blends and Composites*, Chapmann & Hall, London 1994
2. R. T. Sylvest, G. Lancester, S. R. Betso, S.R., *Kautschuk Gummi Kunststoffe* **3**, 186-191 (1997)
3. A. K. Gupta, S. N. Purwar, *J. Applied Polymer Science* 31, 535 (1984)
4. L. Hoffmann, V. Pavšek, M. Schemme, F. Dratschmidt, F. Raue, T. Zysk, G. W. Ehrenstein, *Proceedings 1. Int. Conf. Mechanics of Time Dependent Materials*, Ljubljana 1995, p. 17-22
5. F. Raue, G. W. Ehrenstein, *Proceedings Polymerwerkstoffe*, Merseburg 1996, p. 85-89